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[List of The Appended Documents]

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| [Name of The Document] | Specification | 1 copy |
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| [Name of The Document] | Abstract | 1 copy |
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[Designation of document] Specification

[Title of the Invention] HIGH-MELTING SUPERALLOY AND
METHOD OF PRODUCING THE SAME

[Claims]

[Claim 1] A high-melting superalloy made of iridium or rhodium as a base comprising at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and at least nickel, wherein an fcc phase and an LI_2 phase are formed in a texture thereof.

[Claim 2] The high-melting superalloy according to claim 1, wherein a deposit having an LI_2 structure is conformity-deposited in the fcc phase of the matrix phase.

[Claim 3] The high-melting superalloy according to claim 1 or 2, wherein the volume % of the LI_2 phase is from 20 to 80 %.

[Claim 4] A method of producing the high-melting superalloy described in any of claims 1 to 3, which comprises adding nickel to one of an iridium-base superalloy made of iridium as a base containing from 2 to 22 atomic % of at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base containing from 2 to 22 atomic % of at least one metal selected from said metal group, or to metals or a combination of the alloys realizing one of said superalloys, followed by ingotting to produce a high-melting superalloy.

[Claim 5] The method of producing a high-melting superalloy according to claim 4, wherein the iridium-base superalloy or the rhodium-base superalloy exists in an amount of at least 5 mole % in terms of the superalloy, and nickel is added in an amount of at least 5 atomic %.

[Claim 6] A method of producing the high-melting superalloy described in any of claims 1 to 3, which comprises mixing one of an iridium-base superalloy made of iridium as a base containing from 2 to 22 atomic % of at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base containing from 2 to 22 atomic % of at least one metal selected from said metal group or metals or a combination of alloys realizing one of said superalloys, with a nickel-base alloy made of nickel as a base or metals or a combination of the alloys, followed by ingoting to produce a high-melting superalloy.

[Claim 7] The method of producing a high-melting superalloy according to claim 6, wherein the iridium-base superalloy, the rhodium-base superalloy, or the nickel-base alloy is mixed so that each alloy exists in an amount of at least 5 mole % in terms of each alloy.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a high-melting superalloy. More specifically, the invention relates to a new high-melting superalloy which is capable of improving the output and the heat efficiency of high-temperature instruments such as a gas turbine for electric power generation, a jet engine, a rocket engine, etc.

[0002]

[Prior Art and its Problems]

Turbine blades and turbine vanes used for high-temperature instruments such as a gas turbine for electric power generation, a jet engine, a rocket engine, etc., are used under high-temperature and high-stress conditions. Hitherto, for these turbine blades and turbine vanes, Ni-base superalloys having a high heat resistance and an excellent high-temperature strength have been used but the use temperature have become severe year by year. This is because the increase of a combustion gas temperature is the most effective correspondence to further increase the output and the heat efficiency of high-temperature instruments. Consequently, for the turbine blades and the turbine vanes, the improvement in the high-temperature strength has been desired, which means, in other words, that the improvement in the high-temperature strength of materials used for turbine blades and turbine vanes is indispensable. The durable temperature of Ni-base superalloys capable of having a

substantial strength is about 1,100°C. If a new material, which can be used at a temperature higher than the temperature and can be realized at a relatively low cost, can be developed, it is very useful for practical use.

[0003]

The present invention has been made in view of the circumstances as described above and its object is to provide a new high-melting superalloy which can further improve the output and the heat efficiency of high-temperature instruments, has the characteristics better than the related art Ni-base superalloys, and can be realized at a relatively low cost.

[0004]

[Means for Solving the Problems]

As a result of various investigations, the present inventors have discovered that by compounding or mixing an iridium-base alloy (melting point: 2,447°C) or a rhodium-base alloy (melting point: 1,960°C) having a high-melting point and a high strength at a high temperature and being excellent in the oxidation resistance, with nickel or a nickel-base alloy (density: 8.9 g/cm³ (cf., density of an iridium-base superalloy: 22.4 g/cm³, density of a rhodium-base superalloy: 12.44 g/cm³)), which is light-weight, is excellent in ductility, and is inexpensive as compared with the above-described superalloys, followed by ingotting, a

superalloy wherein both phases of an fcc phase and an LI_2 phase are formed in the texture, and a deposit having an LI_2 structure in the matrix phase having an fcc structure is conformity-deposited is obtained, and that the obtained superalloy is not only excellent in the high-temperature strength and the oxidation resistance but also relatively light-weight and also has a ductility, leading to accomplishment of the present invention.

[0005]

That is, the present invention is to provide a high-melting superalloy comprising at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and at least nickel, wherein an fcc phase and an LI_2 phase are formed in a texture thereof (Claim 1).

[0006]

The invention is to provide, as a preferred embodiment of the above high-melting superalloy that a deposit having an LI_2 structure is conformity-deposited in the fcc phase of the matrix phase (Claim 2) and that the volume % of the LI_2 phase is from 20 to 80 % (Claim 3).

Also, the invention provides a method of producing the high-melting superalloy described in any of claims 1 to 3, which comprises adding nickel to one of an iridium-base superalloy made of iridium as a base containing from 2 to 22

atomic % of at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base containing from 2 to 22 atomic % of at least one metal selected from the metal group, or to metals or a combination of the alloys realizing one of the superalloys, followed by ingoting to produce a high-melting superalloy (Claim 4).

[0007]

As a preferred embodiment for the invention of claim 4, the invention provides a method of producing a high-melting superalloy, wherein the iridium-base superalloy or the rhodium-base superalloy exists in an amount of at least 5 mole % in terms of the superalloy, and nickel is added in an amount of at least 5 atomic % (Claim 5).

Further, the invention provides a method of producing the high-melting superalloy described in any of claims 1 to 3, which comprises mixing one of an iridium-base superalloy made of iridium as a base containing from 2 to 22 atomic % of at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base containing from 2 to 22 atomic % of at least one metal selected from the metal group or metals or a combination of alloys realizing one of the superalloys, with a nickel-base

alloy made of nickel as a base or metals or a combination of the alloys, followed by ingoting to produce a high-melting superalloy (Claim 6).

[0008]

Still further, as a preferred embodiment for the invention of claim 6, the invention provides a method of producing a high-melting superalloy according to claim 6, wherein the iridium-base superalloy, the rhodium-base superalloy, or the nickel-base alloy is mixed so that each alloy exists in an amount of at least 5 mole % in terms of each alloy (Claim 7).

Then, the high-melting superalloy of the invention and the method of producing the same are described in detail.

[0009]

[Mode for Carrying Out the Invention]

The high-melting superalloy according to the invention is a ternary or higher alloy which comprises at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum, and at least nickel wherein an fcc phase and an L1₂ phase are formed in a texture thereof.

[0010]

The high-melting superalloy of the invention is produced by adding nickel to, for example, one of an iridium-base superalloy made of iridium as a base containing

from 2 to 22 atomic % of at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base containing from 2 to 22 atomic % of at least one metal selected from the metal group, or to metals or a combination of the alloys realizing one of the superalloys, followed by ingoting.

[0011]

Also, the high-melting superalloy of the invention is produced by mixing one of an iridium-base superalloy made of iridium as a base containing from 2 to 22 atomic % of at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base containing from 2 to 22 atomic % of at least one metal selected from the metal group or metals or a combination of alloys realizing one of the superalloys, with a nickel-base alloy made of nickel as a base or metals or a combination of the alloys, followed by ingoting.

[0012]

The nickel-base alloy referred to in the latter production method includes from a binary alloy such as a nickel-aluminum (Ni-Al) alloy to a more than binary nickel-base superalloy which is presently used as heat resisting material for high-temperature instruments.

With respect to the ingoting in the production method, there is no particular restriction regarding the system. For example, there is illustrated a method including an arc-melting of the mixture and a homogenizing treatment for homogenizing the composition carried out thereafter as an example.

[0013]

The high-melting superalloys of this invention produced by these production methods each has both phase of the fcc phase and the LI₂ phase in the texture, the formation of the two phases ensure a sufficient strength. It is confirmed by analyzing the phase composition that nichel which is a component element added or blended partially replaces iridium or rhodium in this texture.

[0014]

Also, while it is considered that the composition ratio of the metal components on the superalloy is an important factor, a two-phase conformity texture wherein a deposit having an LI₂ structure, is conformity-deposited in the matrix phase having an fcc structure, is formed. In this case, the two-phase conformity texture means a texture wherein a row of adjacent crystal lattices is continued without being broken. When the two-phase conformity texture is formed, the strength is more increased than the superalloy simply made of two phases of the fcc phase and the LI₂ phase. This is considered to be

caused by that the conformity interface between the matrix phase and the deposit disturbs the transfer of the dislocation. Such a two-phase conformity texture is surely formed in the case where at least one of the iridium-base superalloy and the rhodium-base superalloy, and the nickel-base alloy are used as the raw materials in the above-described production method, and each alloy has a two-phase conformity texture having an fcc phase and an LI_2 phase.

[0015]

It is not always unnecessary that the fcc phase and the LI_2 phase each exists as one kind regarding the kind of constituting substances. Because the high-melting superalloy of the invention is the multi-component alloy as described above, it is possible that plural kinds of the fcc phases and LI_2 phases each having a different existing concentration exist together.

In the texture formed by both phases of the fcc phase and the LI_2 phase, it is preferred that an amount of the LI_2 phase is from 20 to 80% by volume. When the amount of the LI_2 phase is less than the lower limit, the strength is lowered. On the other hand, the LI_2 phase may exceeds the upper limit but the preparation of such a superalloy becomes considerably difficult.

[0016]

Also, in the case where the iridium-base superalloy or the rhodium-base superalloy, and nickel or the nickel-base alloy are used as the raw materials, the high-melting superalloy of the invention can independently show the characteristics of the iridium-base superalloy or the rhodium-base superalloy and nickel or the nickel alloy, in the above-described production method. That is, the high-melting superalloy of the invention shows all the high melting point, the high-temperature high strength, and the excellent oxidation resistance of the iridium-base superalloy or the rhodium-base superalloy and also the light-weight and the excellent ductility of nickel or the nickel-base alloy. Also, by the existence of nickel or the nickel-base alloy, the high-melting superalloy of this invention becomes relatively inexpensive.

[0017]

In this case, in order that the characteristics of these metals, alloys, and the superalloys are clearly observed, it is preferred that a mass ratio of the iridium-base superalloy or the rhodium-base superalloy is at least 5 mole % in terms of superalloy, and the content of nickel alone or the nickel-base alloy is at least 5 mole % in terms of metal or the alloy. When the contents of these superalloys and metal or the alloy are less than the lower limits, these characteristics of them are not always sufficiently obtained.

[0018]

The high-melting superalloy containing from 5 to 50 mole % the iridium-base superalloy or the rhodium-base superalloy of itself or in terms of them is light-weight and is considered to be effective as the rotary members of turbine blades, etc., and, on the other hand, when the content of the iridium-base superalloy or the rhodium-base superalloy is larger than the above-described content, as from 50 to 93%, the application of the high-melting superalloy of the invention to the members used at a higher temperature is expected to be useful.

[0019]

Then, the examples of the high-melting superalloy of the invention and the production method thereof are described.

[0020]

[Example]

Example 1:

An iridium-15 niobium (Ir-15Nb) alloy was compounded with nickel (Ni) and the mixture was arc-melted in a vacuum furnace under an argon atmosphere to produce four kinds of superalloys (ingots) of A, B, C, and D shown in Table 1 below.

[0021]

[Table 1]

| Superalloy | Superalloy Composition (atomic %) | | |
|------------|-----------------------------------|----|---------|
| | Ni | Nb | Ir |
| A | 10 | 15 | Balance |

| | | | |
|---|----|----|---------|
| B | 20 | 15 | Balance |
| C | 30 | 15 | Balance |
| D | 50 | 15 | Balance |

[0022]

From each ingot, a test piece having a height of 6 mm and a diameter of 3 mm was cut and subjected to an aging treatment in a vacuum furnace of 5×10^{-7} Torr at 1,300°C for one week. Also, the phase formed in each test piece was determined by an X-ray diffraction analysis (XRD) and an energy dispersion type X-ray analyzer (EDAX).

As a result, the superalloys A and B of Table 1 had the textures composed of only two phases of the fcc phase and the LI_2 phase. In particular, in the superalloy A, a two-phase conformity texture that the deposit having the LI_2 structure was conformity-deposited in the matrix phase having the fcc structure was formed. The fcc phase was made of Ir and the LI_2 phase was made of Ir_3Nb . Also, in each of these phases, Ni formed a solid solution with the phase. On the other hand, In the superalloys C and D, in addition to the above-described two phases, a δ phase ($(Ir, Ni)_{11}Nb_9$) belonging to a orthorhombic system was confirmed as a third phase. In addition, in each of the superalloys shown above, an amount of Ir_3Nb having the LI_2 structure was within the range of from 20 to 80% by volume.

[0023]

Figs. 1a to 1d each is an optical microphotograph of

each test piece.

In the superalloy A, a dendrite texture (Fig. 1a) was formed and in the superalloys B, C, and D, fine textures (Figs. 1b, 1c, and 1d) were formed. Also, it was confirmed that with the increase of the compounding amount of Ni, the texture became thicker and rougher.

Also, about the above-described test materials, a compression test (in the air, stress speed 3.0×10^{-4} /s) was carried out in the temperature range of from room temperature to 1,200°C. The results are shown in the graph of Fig. 2.

[0024]

As is clear from the graph of Fig. 2, the compression strength of superalloy A was about 2 times that of Ir-15Nb at room temperature and was almost the same as that of Ir-15Nb at 1,200°C. The compression strengths of superalloys B, C, and D were lower than the compression strength of Ir-15Nb at both room temperature and 1,200°C. However, the compression strengths of each of the above superalloys are higher than that of an Ni-base superalloy used for high-temperature instruments.

[0025]

Also, in each of the superalloys, the ductility is improved by the addition of Ni. Particularly, in superalloy B, the ductility is about 13%, which is far higher than that of Ir-15Nb. Also, it is admitted that the utility of the

superalloys is higher than the Ir-15Nb alloy. Furthermore, because a part of Ir is replaced with Ni, the Ir amount of the superalloys can be reduced, which lowers the cost of the alloys. Thus, in the point, the high utility of the superalloys is also confirmed.

Example 2:

As the iridium-base superalloy, an iridium-20 niobium (Ir-20Nb) alloy and an iridium-20 tantalum (Ir-20Ta) alloy were selected and, as the nickel-base alloy, a nickel-16.8 aluminum (Ni-16.8Al) alloy was selected. The mol fractions of the iridium-base superalloy and the nickel-base alloy were selected to be Ir-base superalloy : Ni-base alloy = 25 : 75 (group A), 50 : 50 (group B), and 75 : 25 (group C), sum total 6 kinds of the quaternary alloys of the compositions shown in Table 2 below were prepared by arc-melting in an argon atmosphere.

[0026]

[Table 2]

| | Superalloy Composition (atomic %) | |
|---------|-----------------------------------|-------------------------|
| Group A | Ir-5Nb-62.4Ni-12.6Al | Ir-3.75Ta-62.4Ni-12.6Al |
| Group B | Ir-10Nb-41.6Ni-8.4Al | Ir-7.5Ta-41.6Ni-8.4Al |
| Group C | Ir-15Nb-20.8Ni-4.2Al | Ir-11.25Ta-20.8Ni-4.2Al |

[0027]

About these six kinds of the quaternary alloys, the phase determination and the texture observation as in Example 1 were carried out.

As a result, in the 4 kinds of the superalloys of group

A and group C, the two-phase conformity textures composed of the fcc phase ((Ir, Ni)) and two kinds of LI_2 phases ((Ni, Ir), (Al, Ir) and (Ir, Ni), (Nb, Al), or (Ni, Ir), (Ni, Ta) and (Ir, Ni), (Ta, Al)) were formed. On the other hand, in the two kinds of the superalloys of group B, the two-phase conformity textures by the fcc phase and two kinds of the LI_2 phases same as those of the superalloys of group A and group C were formed but in the cases, B2 phase ((Ir, Ni) (Al, Nb) or (Ir, Ni) (Al, Ta)) was additionally observed.

[0028]

In addition, in the above-described composition formulae, for example, (Ni, Ir), (Al, Nb) means Ni_3Al containing Ir and Nb, wherein a part of Ni is replaced with Ir and a part of Al is replaced with Nb. Other composition formulae also employ the same expression system as above.

Figs. 3a, 3b, and 3c are the secondary electron images showing the textures of Ir-Nb-Ni-Al quaternary alloys belonging to group A, group B, and group C, respectively.

[0029]

In the superalloy A, the fcc phase and the first LI_2 phase of Ni_3Al containing Ir and Nb were observed. In the superalloys B and C, larger LI_2 phases were deposited. The B2 phase was observed in the superalloy B only as described above. In three superalloys A to C, together with the first LI_2 phase of Ni_3Al containing Ir and Nb, a small second LI_2 phase

of Ir_3Nb containing Ni and Al was found in the fcc matrix phase.
[0030]

Then, the alloys prepared were subjected to an aging treatment in vacuo at 1,300°C and 1,400°C for one week and the textures were observed again.

In each superalloy subjected to the aging treatment of 1,300°C, two kinds of small second LI_2 phases were deposited from the fcc matrix phase. As the result of the phase analysis of the superalloys B and C, it was confirmed that the second LI_2 phase contained larger amount of Ni than the first LI_2 phase. In the superalloy A, 23 atomic % Ir was contained in the first LI_2 phase. The Ir amount in the matrix phase increased with the increase of the Ir amount of the superalloy. On the other hand, the Nb amount in the matrix phase is almost the level of 5 atomic %. After the aging treatment at 1,400°C, in addition to a larger first LI_2 phase, a large amount of second LI_2 phases each having a different form and size were formed in the fcc phase. Also, in the superalloy B, the B2 phase was vanished. Thus, it is considered that the melting point of the B2 phase in the superalloy B is 1,400°C. Also, in each of the superalloys, the amount of the LI_2 phase was within the range of from 20 to 80% by volume ratio.

[0031]

The above-described texture observation results were the same as those about the Ir-Ta-Ni-Al quaternary alloy.

Then, each of the following six kinds of the quaternary alloys was heated to 1,400°C for one week, and the compression strength of each of them at 1,200°C was measured. The results are shown as the correlation diagrams of Fig. 4 and Fig. 5.

In theses Fig. 4 and Fig 5, for comparison, the strengths of an Ni-base superalloy (Marm 247) and the iridium-base superalloys of Ir-15Nb and Ir-20Nb are shown together.

[0032]

Each of the quaternary alloys shows the high compression resistance as compared with an Ni-base superalloy applied to high-temperature instruments. On the other hand, the compression strengths of these quaternary alloys are lower than that of Ir-Nb. However, the ductility of each alloy is, by mixing of the nickel-base alloy, 18% at the lowest and is improved as 89% is obtained at the highest. Thus, it is admitted that the utility of the alloys is higher than Ir-15Nb.

[0033]

Also, from Fig. 4, it is confirmed that the compression strength of the quaternary alloy is more improved with the increase of the addition amount of Nb or Ta which is the addition component of the indium-base superalloy.

Example 3:

Four samples having the compositions of $Rh_{85-x}Nb_{15}Ni_x$ ($x = 10, 20, 30, \text{ and } 50$) were prepared by arc-melting and from

each ingot, a test piece of a height of 6 mm and a diameter of 3 mm was cut. The test piece was subjected to an aging treatment in vacuo ($< 10^{-5}$ Pa) at 1,200°C for 100 hours. Also, a compression test (in the air, stress speed 3.0×10^{-4} s $^{-1}$) was carried out at a temperature of from 20 to 1,200°C. Each test piece was heated to the test temperature for from 12 to 20 minutes in a furnace so that a uniform temperature distribution was obtained during the test and kept at the temperature for 5 minutes before the initiation of loading. The compression strength was calculated from the change of the height of each test piece before and after the test.

[0034]

Also, the texture of each superalloy was observed by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The test piece observed by the scanning electron microscope was electron-polished with an ethyl alcohol solution of 5% HCl. The crystal structures and the phase compositions of the superalloys after the heat treatment were determined by an X-ray diffraction analysis (XRD) and an energy dispersion type X-ray analyzer (EDAX).

[0035]

Each of the superalloys of $\text{Rh}_{85-x}\text{Nb}_{15}\text{Ni}_x$ of $x \leq 30$ had the texture composed of only two phases of the fcc phase and the Ll_2 phase of Rh_3Nb containing Ni. Particularly, in the $\text{Rh}_{75}\text{Nb}_{15}\text{Ni}_{10}$ superalloy of $x = 10$, a two-phase conformity

texture that a deposit having the LI_2 structure was conformity-deposited in the matrix phase having the fcc structure was formed. On the other hand, in the $Rh_{35}Nb_{15}Ni_{50}$ superalloy of $x = 50$, a γ'' phase $((Ni, Rh)_3Nb)$ belonging to an orthorhombic system was confirmed. The contents of Ni contained in Rh_3Nb were from 4.8 atomic % of $Rh_{75}Nb_{15}Ni_{10}$ ($x = 10$) to 19.6 atomic % of $Rh_{35}Nb_{15}Ni_{50}$ ($x = 50$). Also, in each superalloy, an amount of the LI_2 phase was within the range of from 20 to 80% by volume.

[0036]

Fig. 6 is the microphotographs of the superalloys heat-treated for 100 hours at 1,200°C.

Figs. 6a to 6d correspond to the compositions of $Rh_{85-x}Nb_{15}Ni_x$ ($x = 10, 20, 30, \text{ and } 50$), respectively, and, in each of the superalloys, a dendrite texture is formed. From the comparison of Figs. 6a to 6d, it is confirmed that with increase of the compounding amount of Ni, the texture becomes coarser as in Example 1.

[0037]

Fig. 7 is a correlation diagram showing the compression strength and the ductility of the $Rh_{85-x}Nb_{15}Ni_x$ superalloys in the relation of the content of nickel. In Fig. 7, the data of the Rh-15 atomic % Nb alloy are shown together for comparison.

At room temperature, each of the superalloys with Ni

added shows a high compression strength as compared with the Rh-Nb two-phase alloy. At 1,200°C, the compression strength of $\text{Rh}_{75}\text{Nb}_{15}\text{Ni}_{10}$ ($x = 10$) is 473 MPa, which is higher than the compression strength of the Rh-Nb two-phase alloy but the compression strength lowers with the increase of the content of Ni. However, the compression strength of each of the superalloys is higher than that of Ni-base superalloys which have hitherto been applied to high-temperature instruments.

[0038]

About the ductility at room temperature, the superalloys with Ni added are equal to that of the Rh-Nb two-phase alloy in the composition on $\text{Rh}_{55}\text{Nb}_{15}\text{Ni}_{30}$ ($x = 30$) but the superalloys having other compositions show lower values. However, the ductility of the superalloys is 11% ($\text{Rh}_{75}\text{Nb}_{15}\text{Ni}_{10}$ ($x = 10$)) at the lowest and have the room-temperature ductility higher than those of the In-base superalloys shown in Example 1.

Example 4:

By following the same procedure as Example 2 except that rhodium was used as the component of constituting the superalloys in place of iridium, superalloys were prepared. The compression strength and the ductility of each superalloy were measured together with the determination of each phase and the observation of each texture. Each of the superalloys obtained shows a high compression strength and an improved

ductility almost the same as those of Example 2 using iridium, as compared with the Ni-base superalloys which have hitherto been used for high-temperature instruments.

[0039]

As a matter of course, the invention is not limited to the above-described examples. That is, about the compositions, the compounding ratios, the preparation methods, etc., of the superalloys, various modifications are possible.

[0040]

[Effect of the Invention]

As described above in detail, according to the present invention, new high-melting superalloys which have the characteristics better than Ni-base superalloys in related art and can be realized at a relatively low cost are provided. Also, by the invention, the more improvements in the output and the heat efficiency of high-temperature instruments can be realized.

[Brief Description of the Drawings]

Figs. 1a, 1b, 1c, and 1d each is an optical microphotograph showing the texture of each sample in Example 1;

Fig. 2 is a bar graph comparing the compression strength and the ductile of each sample in Example 1 with those of Ir-15Nb;

Figs. 3a, 3b, and 3c each is a secondary electron image photograph showing the texture of the In-Nb-Ni-Al quaternary alloy in Example 2;

Fig. 4 is a correlation diagram showing the correlation of the mol fraction of an iridium-base superalloy and the compression strength of the superalloy prepared in Example 2;

Fig. 5 is a correlation diagram showing the correlation of the addition amount of niobium or tantalum in an iridium-base superalloy and the compression strength of the superalloy prepared in Example 2;

Figs. 6a, 6b, 6c, and 6d each is a microphotograph showing the texture of each sample in Example 3;

Fig. 7 is a correlation diagram showing the correlation of the content of nickel in the superalloys prepared in Example 3 to the compression strength and ductile thereof.

[Designation of Document] Abstract

[Abstract]

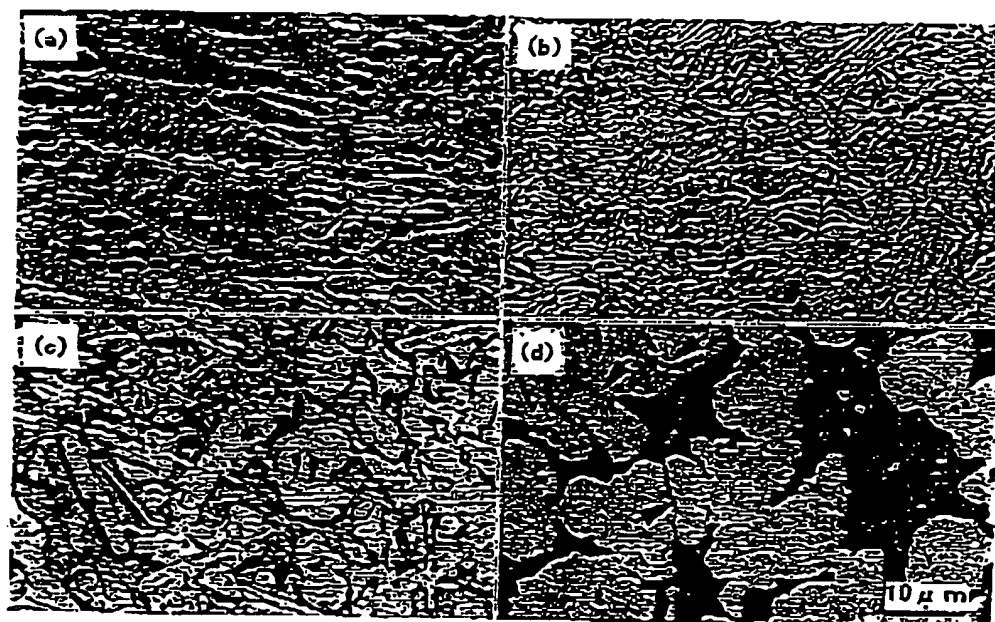
[Problem] To provide a new high melting superalloy which has the characteristics better than the Ni-base superalloy and can be realized at a relatively low cost.

[Means for Resolution] The new iridium- or rhodium-based high-melting superalloy comprises at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and at least nickel wherein an fcc phase and an LI_2 phase are formed in the texture thereof.

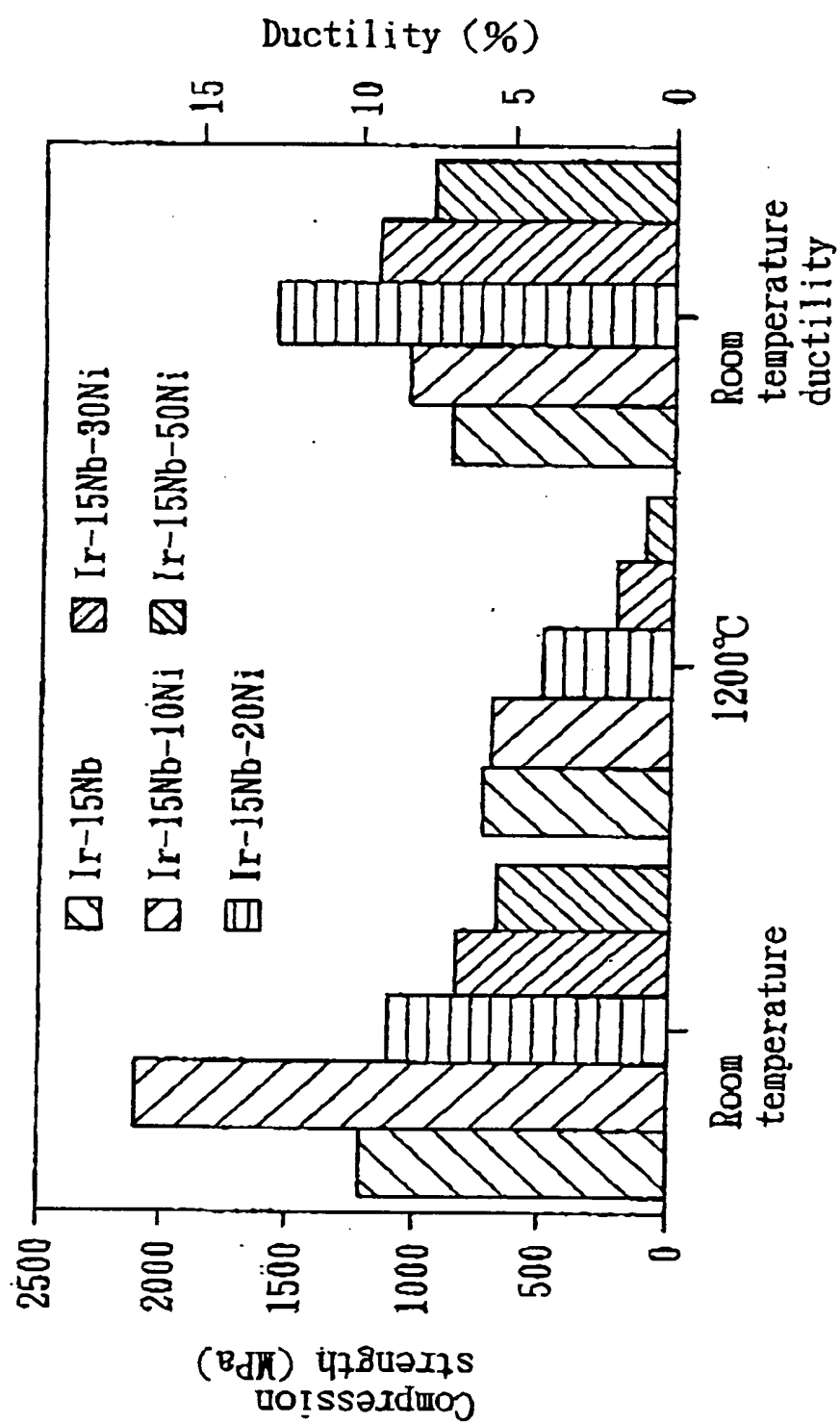
[Selected Drawing] Figure 1

[NAME OF THE DOCUMENT] FIGURE

[Fig. 1]



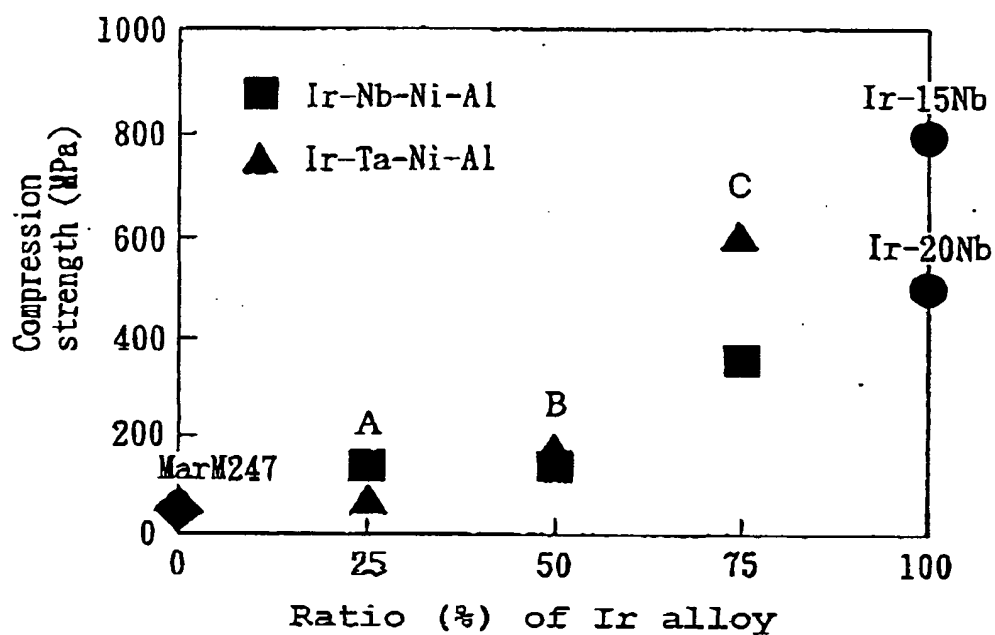
[Fig. 2]



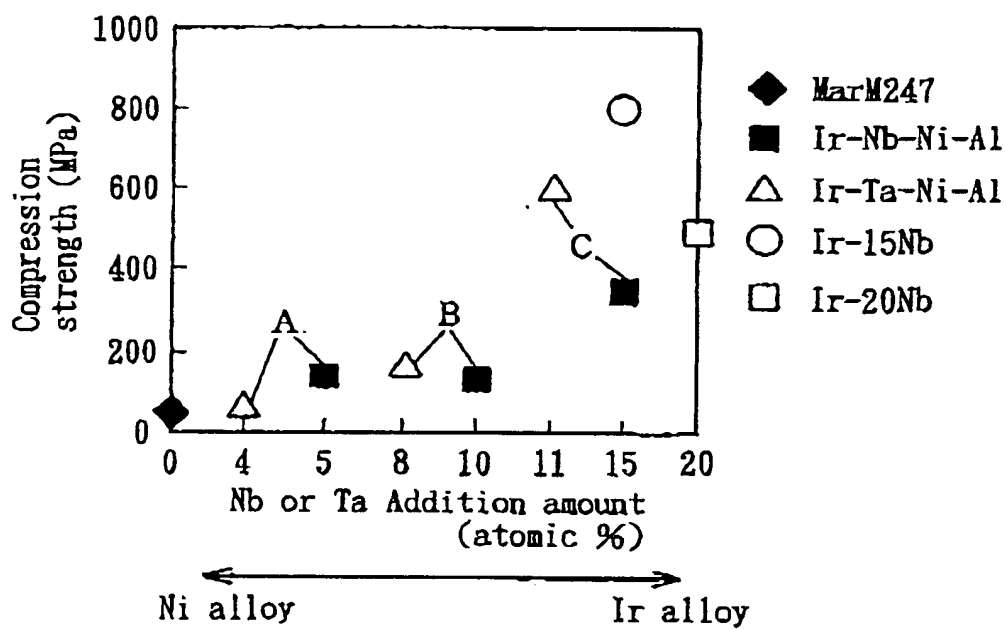
[Fig. 3]



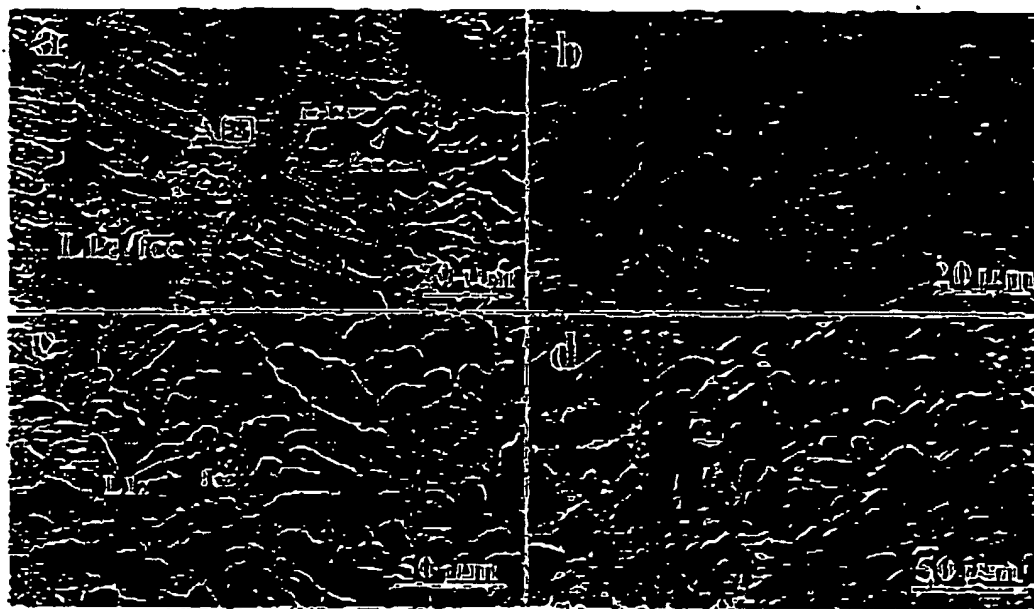
[Fig. 4]



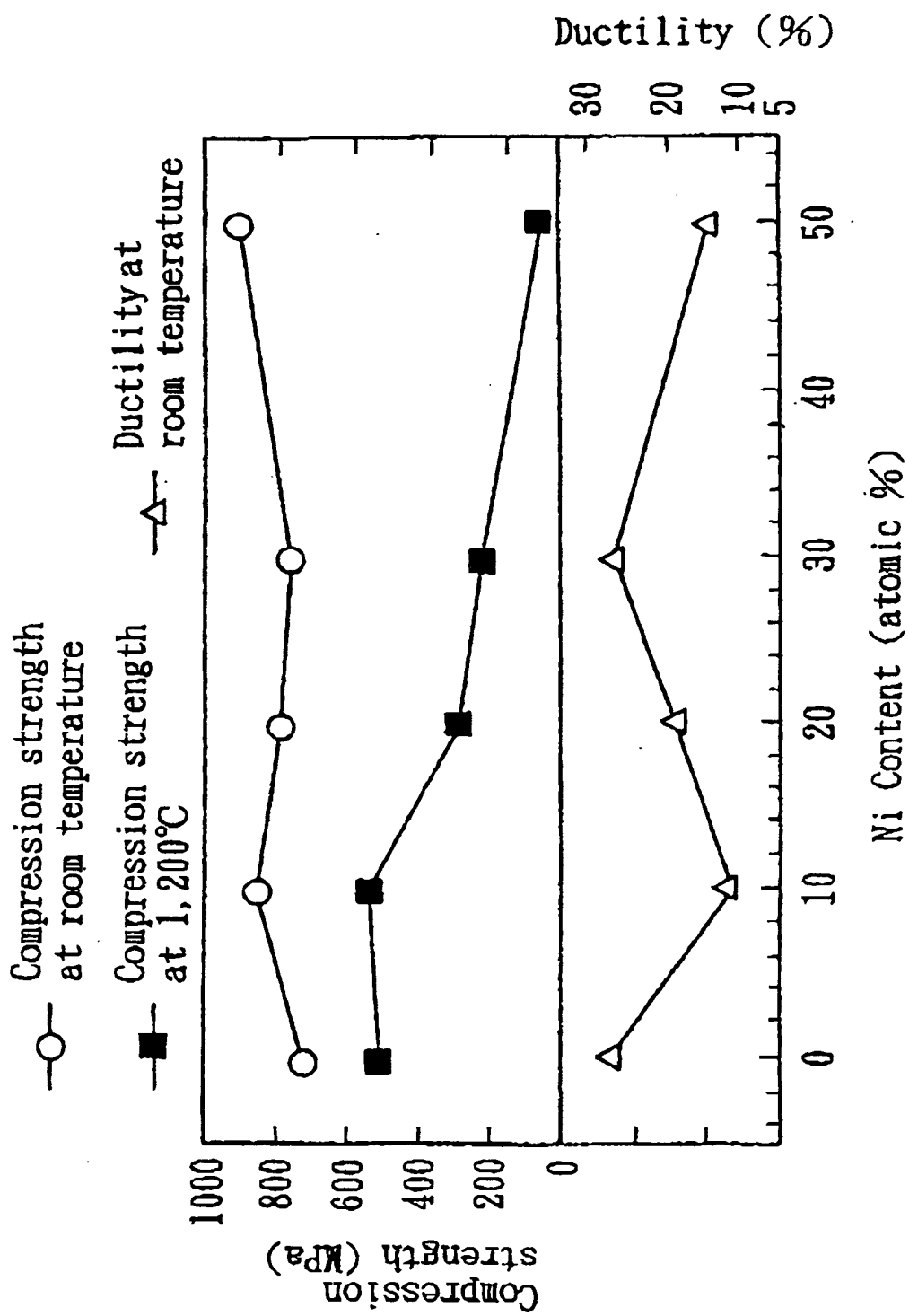
[Fig. 5]



[Fig. 6]



[Fig. 7]



(19)



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(54) **High-melting superalloy and method of producing the same**

Superlegierung mit hoher Schmelztemperatur und Verfahren zu ihrer Herstellung

Superalloyage à température de fusion élevée et procédé pour sa fabrication

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- PATENT ABSTRACTS OF JAPAN vol. 017, no. 259 (C-1061), 21 May 1993 (1993-05-21) -& JP 05 004046 A (SUMITOMO METAL IND LTD), 14 January 1993 (1993-01-14)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 026 269 B1

Description

[0001] The present invention relates to a high-melting superalloy. More specifically, the invention relates to a new high-melting superalloy having an excellent high-temperature strength and a good ductility, which is useful as a material for high-temperature instruments such as a gas turbine for electric power generation, a jet engine, a rocket engine, etc.

[0002] Turbine blades and turbine vanes used for high-temperature instruments such as a gas turbine for electric power generation, a jet engine, a rocket engine, etc., are used under high-temperature and high-stress conditions. Hitherto, for these turbine blades and turbine vanes, Ni-base superalloys having a high heat resistance and an excellent high-temperature strength have been used but the use temperature have become severe year by year. This is because the increase of a combustion gas temperature is most effective to further increase the output and the heat efficiency of high-temperature instruments. Consequently, for the turbine blades and the turbine vanes, the improvement in the high-temperature strength has been desired, which means, in other words, that the improvement in the high-temperature strength of materials used for turbine blades and turbine vanes is indispensable. The durable temperature of Ni-base superalloys capable of having a substantial strength is about 1,100°C. If a new material, which can be used at a temperature higher than the temperature and can be realized at a relatively low cost, can be developed, it is very useful for practical use.

[0003] With respect to Ni-base superalloys having superior high-temperature strength, various investigations have hitherto been made in order to improve an acid resistance, a corrosion resistance, etc. For example, the present inventors have proposed to improve the high-temperature strength and the high-temperature corrosion resistance by solid-solution strengthened Ni-base superalloys in which from 0.1 to 5 atomic % of iridium (Ir) is added, whereby iridium is subjected to solid solution in a γ -phase and a γ' -phase (see Japanese Patent Laid-Open No. 183281/1998 or WO-A-9818972 (EP-A-959143)).

[0004] On the other hand, the present inventors have also already proposed high-melting alloys having two crystal structures, i.e., an FCC structure and an $L1_2$ structure, in which iridium, rhodium or a mixture thereof is added with niobium, tantalum, titanium, aluminum, etc., as alloys having excellent high-temperature strength characteristics and oxidation resistance characteristics (see Japanese Patent Laid-Open No. 311584/1996 or EP-A-732416).

[0005] However, these Ni-base heat-resistant superalloys are lowered in ductility with an improvement in the strength and are troublesome as practically useful heat-resistant materials. Additionally, the prior above iridium-base alloys or rhodium-base alloys are high in cost of the raw materials and involve disadvantages in general-purpose properties. In this sense, the Ni-base superalloys which are relatively cheap and can be easily handled are advantageous.

[0006] However, the related art Ni-base heat-resistant superalloys can not be used at the temperature condition of above 1,300°C as a melting point.

[0007] Precipitations of $L1_2$ phase in fcc phase in matrix were observed in Ir-15Nb-Ni containing superalloys according to "Microstructures and compressive properties of Ir-15Nb refractory superalloy containing Nickel", Scripta Materialica, Vol. 39, No. 6, pp. 723-728, 1998, Elsevier Science Ltd.

[0008] The present invention has been made in view of the circumstances as described above, and the invention relates to a new high-melting superalloy which can further improve the output and the heat efficiency of high-temperature instruments, has the characteristics better in not only high-temperature strength but also ductility than the related art Ni-base superalloys, and can be realized at a relatively low cost.

[0009] As a result of various investigations, the present inventors have discovered that by compounding or mixing an iridium-base alloy (melting point: 2,447°C) or a rhodium-base alloy (melting point: 1,960°C) having a high-melting point and a high strength at a high temperature and being excellent in the oxidation resistance with nickel or a nickel-base alloy (density: 8.9 g/cm³ (cf., density of an iridium-base superalloy: 22.4 g/cm³, density of a rhodium-base superalloy: 12.44 g/cm³)), which is light-weight, is excellent in ductility, and is inexpensive as compared with the above-described superalloys, followed by ingotting, a superalloy wherein both phases of an fcc phase and an $L1_2$ phase are formed in the texture, and a deposit having an $L1_2$ structure in the matrix phase having an fcc structure is conformably deposited is obtained, and that the obtained superalloy is not only excellent in the high-temperature strength and the oxidation resistance but also relatively light-weight and also has a ductility, leading to accomplishment of the present invention.

[0010] That is, a first aspect of the present invention defined in claim 1 is to provide a high-melting superalloy consisting of (A) from 5 to 65 atomic % of nickel and (B) from 5 to 20 atomic % of at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum, with (C) from 30 to 75 atomic % of rhodium, or a mixture of iridium and rhodium, wherein a $L1_2$ phase is precipitated in a fcc phase of the matrix phase, and an amount of the $L1_2$ phase is from 20 to 80% by volume.

[0011] The present invention according to claim 1 also provides a high-melting superalloy consisting of (A) from 5 to 65 atomic % of nickel and (B) from 5 to 20 atomic % of at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium and tantalum with (C) from 30 to 75 atomic % iridium, wherein a $L1_2$ phase is precipitated in a fcc phase of the matrix phase, and an amount of the $L1_2$ phase is from 20 to 80% by volume.

[0012] Also, a second aspect of the invention is to provide the high-melting superalloy according to the first aspect, wherein an atomic ratio of sum of (A) and (B) is from 20 to 70%.

[0013] A third aspect of the invention is to provide the high-melting superalloy according to the first or second aspect, wherein, in case that the metal (c) is iridium, an atomic ratio of (A) to (B) is from 0.3:1 to 8:1.

[0014] A fourth aspect of the invention is to provide the high-melting superalloy according to the first or second aspect, wherein, in case that the metal (C) is rhodium, the atomic ratio of (A) to (B) is from 0.25:1 to 12:1.

[0015] A fifth aspect of the invention as defined in claim 6 is to provide the high-melting superalloy consisting of (A) from 4 to 86 atomic % of nickel, (B) from 0.5 to 20 atomic % of at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium and tantalum, and (C) from 4 to 86 atomic % of iridium or rhodium, or a mixture thereof, with (D) from 0.4 to 20 atomic % of aluminum, wherein a $L1_2$ phase is precipitated in a fcc phase of the matrix phase, and an amount of the $L1_2$ phase is from 20 to 80% by volume.

[0016] The sixth aspect of the invention is to provide the high-melting superalloy according to fifth aspect, wherein the sum of atomic % of (A) and (C), and (B) and (D) are set as follows;

$$(A) + (C) \geq 75 \text{ atomic \%}$$

$$(B) + (D) \leq 25 \text{ atomic \%}$$

[0017] A seventh aspect of the invention is to provide a method of producing a high-melting superalloy as set forth in any of the first to fourth aspects, which comprises compounding at least one of an iridium-base superalloy made of iridium as a base added with at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base added with at least one metal selected from the above-described metal group, with nickel, followed by ingotting to produce a high-melting superalloy.

[0018] An eighth aspect of the invention is to provide a method of producing a high-melting superalloy as set forth in any of the first to sixth aspects, which comprises compounding at least one of an iridium-base superalloy made of iridium as a base added with at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base added with at least one metal selected from the above-described metal group, with a nickel-base alloy made of nickel as a base added with at least one metal selected from the above-described metal group, or aluminum, followed by ingotting to produce a high-melting superalloy.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019]

Figs. 1a, 1b, 1c, and 1d each is an optical microphotograph showing the texture of each sample in Example 1; fig. 2 is a bar graph comparing the compression strength and the ductility of each sample in Example 1 with those of Ir-15Nb;

Figs. 3a, 3b, and 3c each is a secondary electron image photograph showing the texture of the Ir-Nb-Ni-Al quaternary alloy in Example 2;

Fig. 4 is a correlation diagram showing the correlation of the ratio of an iridium-base superalloy and the compression strength of the superalloy prepared in Example 2;

Fig. 5 is a correlation diagram showing the correlation of the addition amount of niobium or tantalum in an iridium-base superalloy and the compression strength of the superalloy prepared in Example 2;

Figs. 6a, 6b, 6c, and 6d each is a microphotograph showing the texture of each sample in Example 3;

Fig. 7 is a correlation diagram showing the correlation of the content of nickel in the superalloys prepared in Example 3 to the compression strength and ductile thereof;

Fig. 8 is a view showing the compression ductility and yield strengths at room-temperature and at 1473K of superalloys of the invention containing Rh and Ir;

Fig. 9 is a photograph showing a fracture surface of the superalloy of the invention; and

Fig. 10 is a photograph showing the texture of the superalloy of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0020] Then, the high-melting superalloy of the invention and the method of producing the same are described in

detail.

[0021] The high-melting superalloy according to the invention consists of (A) from 5 to 73 atomic % of nickel and (B) from 2 to 22 atomic % of at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium and tantalum, with (C) a balance of rhodium, or a mixture of iridium and rhodium, wherein an fcc phase and a L_{12} phase are formed in a texture thereof and the L_{12} phase is precipitated in a fcc phase of the matrix phase, and an amount of the L_{12} phase is from 20 to 80% by volume.

[0022] Alternatively, the high-melting superalloy according to the invention consists of (A) from 5 to 73 atomic % of nickel and (B) from 2 to 22 atomic % of at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium and tantalum, with (C) a balance of iridium, wherein an fcc phase and a L_{12} phase are formed in a texture thereof and the L_{12} phase is precipitated in a fcc phase of the matrix phase, and an amount of the L_{12} phase is from 20 to 80% by volume.

[0023] Needless to say, it is acceptable that inevitable impurities mingled in the raw materials during the production or in the production steps are present in this composition.

[0024] A proportion of the component (C), i.e., iridium or rhodium, or a mixture thereof, to be contained as a balance is substantially from 30 to 75 atomic %.

[0025] In the case where, in the high-melting superalloy of the invention, the components (A), (B) and (C) fall out the above-described composition range, the requirements which are indispensable to the composition of the superalloy of the invention, (1) a L_{12} structure is precipitated in the matrix phase having an fcc structure; and (2) the precipitation phase having an L_{12} structure accounts for from 20 to 80% by volume, cannot be met. Hence, in this case, not only a desired high-temperature strength but also an improvement in the ductility cannot be obtained.

[0026] In the invention, in order to attain an excellent high-temperature strength and an improvement in the ductility, it is preferred that a sum of atomic % of (A) and (B) is from 20 to 70% and that, in case of iridium as metal (C), an atomic ratio of the component (A) to the component (B) is from 0.3:1 to 8:1. It is further preferred that, in case of rhodium as metal (C), the atomic ratio of the component (A) to the component (B) is from 0.25:1 to 12:1.

[0027] Of titanium, zirconium, hafnium, vanadium, niobium, and tantalum as the component (C) are particularly preferred niobium, tantalum and titanium.

[0028] These high-melting superalloys are produced by mixing the alloy-constituting element materials so as to obtain a specified composition, followed by ingoting, and more actually, by compounding at least one of an iridium-base superalloy made of iridium as a base added with at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base added with at least one metal selected from the above-described metal group, with nickel, followed by ingoting.

[0029] Also, these high-melting superalloys are produced by mixing at least one of an iridium-base superalloy made of iridium as a base added with at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base added with at least one metal selected from the above-described metal group, with a nickel-base alloy made of nickel as a base added with at least one metal selected from the above-described metal group, followed by ingoting.

[0030] In the invention, aluminum may further be added as the component. In this case, the high-melting superalloy of the present invention comprises

(A) from 4 to 86 atomic % of nickel,

(B) from 0.5 to 20 atomic % of at least one metal selected from the group consisting of Ti, Zr, Hf, V, Nb, and Ta, and

(C) from 4 to 86 atomic % of Ir or Rh, or a mixture thereof, with

(D) from 0.4 to 20 atomic % of Al.

[0031] It is preferred that the sum of atomic % of (A) and (C), and (B) and (D) are set as follows;

$$(A) + (C) \geq 75 \text{ atomic \%}$$

$$(B) + (D) \leq 25 \text{ atomic \%}$$

[0032] In producing the aluminum-containing alloys, nickel-aluminum (Ni-Al) alloys which are presently used as heat-resisting materials for high-temperature instruments are useful as the above-described nickel-base alloy.

[0033] With respect to the ingoting in the production method, there is no particular restriction regarding the system. For example, there is illustrated a method including an arc-melting of the mixture and a homogenizing treatment, such as heat-treatment at high temperature condition of about 1,800°C and below for homogenizing the composition carried out thereafter as an example.

[0034] The high-melting superalloys of this invention produced by these production methods each has both phase of the fcc phase and the $L1_2$ phase in the texture.

[0035] Also, while it is considered that the composition ratio of the metal components on the superalloy is an important factor, a two-phase conformity texture wherein a deposit having an $L1_2$ structure, is conformity-deposited in the matrix phase having an fcc structure, is formed. In this case, the two-phase conformity texture means a texture wherein a row of adjacent crystal lattices is continued without being broken. When the two-phase conformity texture is formed, the strength is more increased than the superalloy simply made of two phases of the fcc phase and the $L1_2$ phase. This is considered to be caused by that the conformity interface between the matrix phase and the deposit disturbs the transfer of the dislocation. Such a two-phase conformity texture is surely formed in the case where at least one of the iridium-base superalloy and the rhodium-base superalloy, and the nickel-base alloy are used as the raw materials in the above-described production method, and each alloy has a two-phase conformity texture having an fcc phase and an $L1_2$ phase.

[0036] It is not always unnecessary that the fcc phase and the $L1_2$ phase each exists as one kind regarding the kind of constituting substances. Because the high-melting superalloy of the invention is the multi-component alloy as described above, it is possible that plural kinds of the fcc phases and $L1_2$ phases each having a different existing concentration exist together.

[0037] In the texture formed by both phases of the fcc phase and the $L1_2$ phase, the amount of the $L1_2$ phase is from 20 to 80% by volume. When the amount of the $L1_2$ phase is less than the lower limit, the strength is lowered. On the other hand, the $L1_2$ phase may exceeds the upper limit but the preparation of such a superalloy becomes considerably difficult.

[0038] Also, in the case where the iridium-base superalloy or the rhodium-base superalloy, and nickel or the nickel-base alloy are used as the raw materials, the high-melting superalloy of the invention can independently show the characteristics of the iridium-base superalloy or the rhodium-base superalloy and nickel or the nickel alloy, in the above-described production method. That is, the high-melting superalloy of the invention shows all the high melting point, the high-temperature high strength, and the excellent oxidation resistance of the iridium-base superalloy or the rhodium-base superalloy and also the light-weight and the excellent ductility of nickel or the nickel-base alloy. Also, by the existence of nickel or the nickel-base alloy, the high-melting superalloy of this invention becomes relatively inexpensive.

[0039] The high-melting superalloy containing 50 atomic % and below of the iridium-base superalloy or the rhodium-base superalloy of itself or in terms of them is light-weight and is considered to be effective as the rotary members of turbine blades, etc., and on the other hand, when the content of the iridium-base superalloy or the rhodium-base superalloy is larger than the above-described content, as 50 % and above, the application of the high-melting superalloy of the invention to the members used at a higher temperature is expected to be useful.

[0040] Then, the examples of the high-melting superalloy of the invention and the production method thereof are described.

Reference Example 1:

[0041] An iridium-15 niobium (Ir-15Nb) alloy was compounded with nickel (Ni) and the mixture was arc-melted in a vacuum furnace under an argon atmosphere to produce four kinds of superalloys (ingots) of A, B, C, and D shown in Table 1 below,

Table 1

| Superalloy | Superalloy Composition (atomic %) | | |
|------------|-----------------------------------|----|---------|
| | Ni | Nb | Ir |
| A | 10 | 15 | Balance |
| B | 20 | 15 | Balance |
| C | 30 | 15 | Balance |
| D | 50 | 15 | Balance |

[0042] From each ingot, a test piece having a height of 6 mm and a diameter of 3 mm was cut and subjected to an aging treatment in a vacuum furnace of 5×10^{-7} Torr at 1,300°C for one week. Also, the phase formed in each test piece was determined by an X-ray diffraction analysis (XRD) and an energy dispersion type X-ray analyzer (EDAX).

[0043] As a result, the superalloys A and B of Table 1 had the textures composed of only two phases of the fcc phase and the $L1_2$ phase. In particular, in the superalloy A, a two-phase conformity texture that the precipitation having the $L1_2$ structure was conformity-precipitated in the matrix phase having the fcc structure was formed. The fcc phase was

made of Ir and the Li_2 phase was made of Ir_3Nb . Also, in each of these phases, Ni formed a solid solution with the phase. On the other hand, in the superalloys C and D, in addition to the above-described two phases, a δ phase ($(Ir, Ni)_{11}Nb_9$) belonging to a orthorhombic system was confirmed as a third phase. In addition, in each of the superalloys shown above, an amount of Ir_3Nb having the Li_2 structure was within the range of from 20 to 80% by volume.

[0044] Figs. 1a to 1d each is an optical microphotograph of each test piece.

[0045] In the superalloy A, a dendrite texture (Fig. 1a) was formed and in the superalloys B, C, and D, fine textures (Figs. 1b, 1c, and 1d) were formed. Also, it was confirmed that with the increase of the compounding amount of Ni, the texture became thicker and rougher.

[0046] Also, about the above-described test materials, a compression test (in the air, stress speed 3.0×10^{-4} /s) was carried out in the temperature range of from room temperature to $1,200^\circ\text{C}$. The results are shown in the graph of Fig. 2.

[0047] As is clear from the graph of Fig. 2, the compression strength of superalloy A was about 2 times that of Ir-15Nb at room temperature and was almost same as that of Ir-15Nb at $1,200^\circ\text{C}$. The compression strengths of superalloys B, C, and D were lower than the compression strength of Ir-15Nb at both room temperature and $1,200^\circ\text{C}$. However, the compression strengths of each of the above superalloys are higher than that of an Ni-base superalloy used for high-temperature instruments.

[0048] Also, in each of the superalloys, the ductility is improved by the addition of Ni. Particularly, in superalloy B, the ductility is about 13%, which is far higher than that of Ir-15Nb. Also, it is admitted that the utility of the superalloys is higher than the Ir-15Nb alloy. Furthermore, because a part of Ir is replaced with Ni, the Ir amount of the superalloys can be reduced, which lowers the cost of the alloys. Thus, in the point, the high utility of the superalloys is also confirmed.

Example 2:

[0049] As the Iridium-base superalloy, an iridium-20 niobium (Ir-20Nb) alloy and an iridium-20 tantalum (Ir-20Ta) alloy were selected and, as the nickel-base alloy, a nickel-16.8 aluminum (Ni-16.8Al) alloy was selected. The mol fractions of the Iridium-base superalloy and the nickel-base alloy were selected to be Ir-base superalloy : Ni-base alloy = 25 : 75 (group A), 50 : 50 (group B), and 75 : 25 (group C), sum total 6 kinds of the quaternary alloys of the compositions shown in Table 2 below were prepared by arc-melting in an argon atmosphere.

Table 2

| | Superalloy Composition (atomic %) | |
|---------|-----------------------------------|-------------------------|
| Group A | Ir-5Nb-62.4Ni-12.6Al | Ir-3.75Ta-62.4Ni-12.6Al |
| Group B | Ir-10Nb-41.6Ni-8.4Al | Ir-7.5Ta-41.6Ni-8.4Al |
| Group C | Ir-15Nb-20.8Ni-4.2Al | Ir-11.25Ta-20.8Ni-4.2Al |

[0050] About these 6 kinds of the quaternary alloys, the phase determination and the texture observation as in Example 1 were carried out.

[0051] As a result, in the 4 kinds of the superalloys of group A and group C, the two-phase conformity textures composed of the fcc phase ((Ir, Ni)) and 2 kinds of Li_2 phases ((Ni, Ir) , (Al, Ir) and (Ir, Ni) (Nb, Al), or (Ni, Ir) , (Ni, Ta) and (Ir, Ni) (Ta, Al)) were formed. On the other hand, in the 2 kinds of the superalloys of group B, the two-phase conformity textures by the fcc phase and 2 kinds of the Li_2 phases same as those of the superalloys of group A and group C were formed but in the cases, B2 phase ((Ir, Ni) (Al, Nb) or (Ir, Ni) (Al, Ta)) was additionally observed.

[0052] In addition, in the above-described composition formulae, for example, $(Ni, Ir)_3 (Al, Nb)$ means Ni_3Al containing Ir and Nb, wherein a part of Ni is replaced with Ir and a part of Al is replaced with Nb. Other composition formulae also employ the same expression system as above.

[0053] Figs. 3a, 3b, and 3c are the secondary electron images showing the textures of Ir-Nb-Ni-Al superalloys belonging to group A, group B, and group C, respectively.

[0054] In the superalloy A, the fcc phase and the first Li_2 phase of Ni_3Al containing Ir and Nb were observed. In the superalloys B and C, larger Li_2 phases were deposited. The B2 phase was observed in the superalloy B only as described above. In three superalloys A to C, together with the first Li_2 phase of Ni_3Al containing Ir and Nb, a small second Li_2 phase of Ir_3Nb containing Ni and Al was found in the fcc matrix phase.

[0055] Then, the alloys prepared were subjected to an aging treatment in vacuo at $1,300^\circ\text{C}$ and $1,400^\circ\text{C}$ for one week and the textures were observed again.

[0056] In each superalloy subjected to the aging treatment of $1,300^\circ\text{C}$, 2 kinds of small second Li_2 phases were precipitated from the fcc matrix phase. As the result of the phase analysis of the superalloys B and C, it was confirmed that the second Li_2 phase contained larger amount of Ni than the first Li_2 phase. In the superalloy A, 23 atomic % Ir was contained in the first Li_2 phase. The Ir amount in the matrix phase increased with the increase of the Ir amount of

the superalloy. On the other hand, the Nb amount in the matrix phase is almost the level of 5 atomic %. After the aging treatment at 1,400°C, in addition to a larger $L1_2$ phase, a large amount of second $L1_2$ phases each having a different form and size were formed in the fcc phase. Also, in the superalloy B, the B2 phase was vanished. Thus, it is considered that the melting point of the B2 phase in the superalloy B is 1,400°C. Also, in each of the superalloys, an amount of the $L1_2$ phase was within the range of from 20 to 80% by volume ratio.

[0057] The above-described texture observation results were the same as those about the Ir-Ta-Ni-Al quaternary alloy.

[0058] Then, each of the following 6 kinds of the quaternary alloys was heated to 1,400°C for one week, and the compression strength of each of them at 1,200°C was measured. The results are shown as the correlation diagrams of Fig. 4 and Fig. 5.

[0059] In these Fig. 4 and Fig. 5, for comparison, the strengths of an Ni-base superalloy (Marr 247) and the iridium-base superalloys of Ir-15Nb and Ir-20Nb are shown together.

[0060] Each of the quaternary alloys shows the high compression resistance as compared with an Ni-base superalloy applied to high-temperature instruments. On the other hand, the compression strengths of these quaternary alloys are lower than that of Ir-Nb. However, the ductility of each alloy is, by mixing of the nickel-base alloy, 18% at the lowest and is improved as 89% is obtained at the highest. Thus, it is admitted that the utility of the alloys is higher than Ir-15Nb.

[0061] Also, from Fig. 4, it is confirmed that the compression strength of the quaternary alloy is more improved with the increase of the addition amount of Nb or Ta which is the addition component of the iridium-base superalloy.

Example 3:

[0062] Four samples having the compositions of $Rh_{85-x}Nb_{15}Ni_x$ ($x = 10, 20, 30$, and 50) were prepared by arc-melting and from each ingot, a test piece of a height of 6 mm and a diameter of 3 mm was cut. The test piece was subjected to an aging treatment in vacuo ($< 10^{-5}$ Pa) at 1,200°C for 100 hours. Also, a compression test (In the air, stress speed $3.0 \times 10^{-4} s^{-1}$) was carried out at a temperature of from 20 to 1,200°C. Each test piece was heated to the test temperature for from 12 to 20 minutes in a furnace so that a uniform temperature distribution was obtained during the test and kept at the temperature for 5 minutes before the initiation of loading. The compression strength was calculated from the change of the height of each test piece before and after the test.

[0063] Also, the texture of each superalloy was observed by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The test piece observed by the scanning electron microscope was electron-polished with an ethyl alcohol solution of 5% HCl. The crystal structures and the phase compositions of the superalloys after the heat treatment were determined by an X-ray diffraction analysis (XRD) and an energy dispersion type X-ray analyzer (EDAX).

[0064] Each of the superalloys of $Rh_{85-x}Nb_{15}Ni_x$ of $x \leq 30$ had the texture composed of only 2 phases of the fcc phase and the $L1_2$ phase of Rh_3Nb containing Ni. Particularly, in the $Rh_{75}Nb_{15}Ni_{10}$ superalloy of $x = 10$, a two-phase conformity texture that a deposit having the $L1_2$ structure was conformity-deposited in the matrix phase having the fcc structure was formed. On the other hand, in the $Rh_{95}Nb_{15}Ni_{30}$ superalloy of $x = 50$, a γ' phase ((Ni, Rh) $_3$ Nb) belonging to an orthorhombic system was confirmed. The contents of Ni contained in Rh_3Nb were from 48 atomic % of $Rh_{75}Nb_{15}Ni_{10}$ ($x = 10$) to 19.6 atomic % of $Rh_{35}Nb_{15}Ni_{50}$ ($x = 50$). Also, in each superalloy, an amount of the $L1_2$ phase precipitated in fcc matrix phase was within the range of from 20 to 80% by volume.

[0065] Fig. 6 is the microphotographs of the superalloys heat-treated for 100 hours at 1,200°C.

[0066] Figs. 6a to 6d correspond to the compositions of $Rh_{85-x}Nb_{15}Ni_x$ ($x = 10, 20, 30$, and 50), respectively, and, in each of the superalloys, a dendrite texture is formed. From the comparison of Figs. 6a to 6d, it is confirmed that with increase of the compounding amount of Ni, the texture becomes coarser as in Example 1.

[0067] Fig. 7 is a correlation diagram showing the compression strength and the ductility of the $Rh_{85-x}Nb_{15}Ni_x$ superalloys in the relation of the content of nickel. In Fig. 7, the data of the Rh-15 atomic % Nb alloy are shown together for comparison.

[0068] At room temperature, each of the superalloys with Ni added shows a high compression strength as compared with the Rh-Nb two-phase alloy. At 1,200°C, the compression strength of $Rh_{75}Nb_{15}Ni_{10}$ ($x = 10$) is 473 MPa, which is higher than the compression strength of the Rh-Nb two-phase alloy but the compression strength lowers with the increase of the content of Ni. However, the compression strength of each of the superalloys is higher than that of Ni-base superalloys which have hitherto been applied to high-temperature instruments.

[0069] About the ductility at room temperature, the superalloys with Ni added are equal to that of the Rh-Nb two-phase alloy in the composition on $Rh_{55}Nb_{15}Ni_{30}$ ($x = 30$) but the superalloys having other compositions show lower values. However, the ductility of the superalloys is 11% ($Rh_{75}Nb_{15}Ni_{10}$ ($x = 10$)) at the lowest and have the room-temperature ductility higher than those of the Ir-base superalloys shown in Example 1.

Example 4:

[0070] By following the same procedure as Example 2 except that rhodium was used as the component of constituting the superalloys in place of iridium, superalloys were prepared. The compression strength and the ductility of each superalloy were measured together with the determination of each phase and the observation of each texture. Each of the superalloys obtained shows a high compression strength and an improved ductility almost the same as those of Example 2 using iridium, as compared with the Ni-base superalloys which have hitherto been used for high-temperature instruments.

Example 5:

[0071] By following the same procedure as in Example 1, the alloys of the following 2 kinds of compositions (atomic %) were produced.

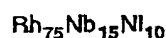


[0072] About the 2 kinds of the alloys, the compression strengths (at room temperature and at 1,200°C) and the room-temperature compressive strain were measured, they were compared with those of the high-temperature superalloys of $\text{Rh}_{75}\text{Nb}_{15}\text{Ni}_{10}$ and $\text{Ir}_{75}\text{Nb}_{15}\text{Ni}_{10}$ and also those of the alloy of Ir-Nb₁₅ of related art, and the results are shown in Fig. 8.

[0073] From Fig. 8, it can be seen that in the superalloys of this invention containing both Rh and Ir, at room temperature, the compression strength is about 2 times that of the binary alloy of Ir-Nb₁₅, at 1,200°C, the compression strength is almost same as that of the binary alloy, that is, the high-temperature compression strength is not lowered. Also, it can be seen that the room-temperature compressive strain is more improved as the amount of Rh becomes larger.

[0074] Fig. 9 and Fig. 10 are the photographs observing the rupture cross-sections of the alloys and the photographs showing the alloy textures of them, and the alloys are as follows:

a:



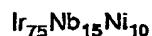
b:



c:



d:



[0075] From Fig. 9, it was confirmed that each alloy showed a transgranular rupture and improved the brittle property of the Ir-Nb binary alloy caused by an intergranular rupture.

[0076] From Fig. 10, it was confirmed that in each case, a third phase was not formed and the texture of each alloy was a two-phase texture of fcc + L₁₂.

[0077] As a matter of course, the invention is not limited to the above-described examples. That is, about the compositions, the compounding ratios, the preparation methods, etc., of the superalloys, various modifications are possible.

[0078] As described above in detail, according to the present invention, new high-melting superalloys which have the characteristics better than Ni-base superalloys in related art and can be realized at a relatively low cost are provided. Also, by the invention, the more improvements in the output and the heat efficiency of high-temperature instruments can be realized.

Claims

1. A high-melting superalloy consisting of:

(A) from 5 to 65 atomic % of nickel; and either

(B) from 5 to 20 atomic % of at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum, with (C) from 30 to 75 atomic % of rhodium, or a mixture of iridium and rhodium; or

(B) from 5 to 20 atomic % of at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium and tantalum, with (C) from 30 to 75 atomic % of iridium;

wherein a Li_2 phase precipitated in a fcc phase of the matrix phase, and the amount of the Li_2 phase is from 20 to 80% by volume.

2. The high-melting superalloy of claim 1 wherein metal (B) is selected from titanium, zirconium, hafnium, vanadium and tantalum.

3. The high-melting superalloy according to claim 1 or 2, wherein the atomic % of sum of (A) and (B) is from 20 to 70%.

4. The high-melting superalloy according to claim 1 to 3, wherein, in case that the metal (C) is iridium; the atomic ratio of (A) to (B) is from 0.3:1 to 8:1.

5. The high-melting superalloy according to claim 1 to 3, wherein, in case that the metal (C) is rhodium, the atomic ratio of (A) to (B) is from 0.25:1 to 12:1.

6. A high-melting superalloy consisting of (A) from 4 to 86 atomic % of nickel, (B) from 0.5 to 20 atomic % of at least one metal selected from the group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum, and (C) from 4 to 86 atomic % of iridium or rhodium, or a mixture thereof, with (D) from 0.4 to 20 atomic % of aluminum, wherein a Li_2 phase is precipitated in a fcc phase of the matrix phase, and the amount of the Li_2 phase is from 20 to 80% by volume.

7. The high-melting superalloy according to claim 6, wherein the sum of atomic % of (A) and (C), and (B) and (D) are set as follows.

$$(A) + (C) \geq 75 \text{ atomic \%}$$

$$(B) + (D) \leq 25 \text{ atomic \%}$$

8. A method of producing a high-melting superalloy as set forth in any of claims 1 to 5, which comprises compounding at least one of an iridium-base superalloy made of iridium as a base added with at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base added with at least one metal selected from the above-described metal group, with nickel, followed by ingotting to produce a high-melting superalloy.

9. A method of producing a high-melting superalloy as set forth in any of claims 1 to 7, which comprises compounding at least one of an iridium-base superalloy made of iridium as a base added with at least one metal selected from the metal group consisting of titanium, zirconium, hafnium, vanadium, niobium, and tantalum and a rhodium-base superalloy made of rhodium as a base added with at least one metal selected from the above-described metal

group, with a nickel-base alloy made of nickel as a base added with at least one metal selected from the above-described metal group, or aluminum, followed by ingoting to produce a high-welding superalloy.

5 Patentansprüche

1. Hochschmelzende Superlegierung bestehend aus

(A) von 5 bis 65 Atom-% Nickel; und entweder

(B) von 5 bis 20 Atom-% aus wenigstens einem Metall ausgewählt aus der Gruppe, die besteht aus Titan, Zirkonium, Hafnium, Vanadium, Niob und Tantal mit

(C) von 30 bis 75 Atom-% Rhodium oder einem Gemisch von Iridium und Rhodium; oder

(B) von 5 bis 20 Atom-% aus wenigstens einem Metall ausgewählt aus der Gruppe, die besteht aus Titan, Zirkonium, Hafnium, Vanadium und Tantal mit (C) von 30 bis 75 Atom-% Iridium;

worin eine Li_2 Phase sich in einer fcc Phase der Matrixphase niederschlägt und die Menge der Li_2 Phase von 20 bis 80 Volumen-% reicht.

2. Die hochschmelzende Superlegierung gemäß Anspruch 1, worin Metall (B) ausgewählt wird aus Titan, Zirkonium, Hafnium, Vanadium und Tantal.

3. Die hochschmelzende Superlegierung gemäß Anspruch 1 oder 2, worin die Atom-% der Summe von (A) und (B) von 20 bis 70 % reichen.

4. Die hochschmelzende Superlegierung gemäß Anspruch 1 bis 3, worin für den Fall das das Metall (C) Iridium ist, das Atomverhältnis von (A) zu (B) von 0,3:1 bis 8:1 reicht.

5. Die hochschmelzende Superlegierung gemäß Anspruch 1 bis 3, worin für den Fall das das Metall (C) Rhodium ist, das Atomverhältnis von (A) zu (B) von 0,25:1 bis 12:1 reicht.

6. Hochschmelzende Superlegierung bestehend aus

(A) von 4 bis 86 Atom-% Nickel,

(B) von 0,5 bis 20 Atom-% aus wenigstens einem Metall ausgewählt aus der Gruppe, die besteht aus Titan, Zirkonium, Hafnium, Vanadium, Niob und Tantal und

(C) von 4 bis 86 Atom-% Iridium oder Rhodium, oder einem Gemisch davon, mit

(D) von 0,4 bis 20 Atom-% Aluminium,

worin eine Li_2 Phase in einer fcc Phase der Matrixphase gefällt wird und die Menge der Li_2 Phase von 20 bis 80 Volumen-% reicht.

7. Die hochschmelzende Superlegierung gemäß Anspruch 6, worin sich die Summe der Atom-% von (A) und (C), und (B) und (D) sich wie folgt darstellt:

$$(A) + (C) \geq 75 \text{ Atom-\%}$$

$$(B) + (D) \leq 25 \text{ Atom-\%}.$$

8. Ein Verfahren zur Herstellung einer hochschmelzenden Superlegierung wie in einem der Ansprüche 1 bis 5 dargestellt, welches umfasst das Vermischen wenigstens einer Superlegierung auf Iridium-Basis, hergestellt aus Iridium als einer Basis angereichert mit wenigstens einem Metall ausgewählt aus der Metallgruppe bestehend aus Titan, Zirkonium, Hafnium, Vanadium, Niob und Tantal, und einer Superlegierung auf Rhodium-Basis, hergestellt aus Rhodium als einer Basis angereichert mit wenigstens einem Metall ausgewählt aus der oben beschriebenen Metallgruppe,

mit Nickel, gefolgt von einem Guss in Blöcke um eine hochschmelzende Superlegierung herzustellen.

9. Ein Verfahren zur Herstellung einer hochschmelzenden Superlegierung wie in einem der Ansprüche 1 bis 7 dargelegt, welches umfasst das Vermischen wenigstens einer Superlegierung auf Iridium-Basis, hergestellt aus Iridium als einer Basis angereichert mit wenigstens einem Metall ausgewählt aus der Metallgruppe bestehend aus Titan, Zirkonium, Hafnium, Vanadium, Niob und Tantal, und einer Superlegierung auf Rhodium-Basis, hergestellt aus Rhodium als einer Basis angereichert mit wenigstens einem Metall ausgewählt aus der oben beschriebenen Metallgruppe, mit einer Legierung auf Nickel-Basis, hergestellt aus Nickel als einer Basis angereichert mit wenigstens einem Metall ausgewählt aus der oben beschriebenen Metallgruppe, oder Aluminium, gefolgt von einem Guss in Blöcke um eine hochschmelzende Superlegierung herzustellen.

Revendications

1. Superalloyage à température de fusion élevée constitué de :

(A) 5 à 65 % atomiques de nickel ; et soit de

(B) 5 à 20 % atomiques d'au moins un métal choisi dans le groupe constitué par le titane, le zirconium, le hafnium, le vanadium, le niobium, et le tantale, avec (C) de 30 à 75 % atomiques de rhodium, ou d'un mélange d'iridium et de rhodium ; soit de

(B) de 5 à 20 % atomiques d'au moins un métal choisi dans le groupe constitué par le titane, le zirconium, le hafnium, le vanadium, et le tantale, avec (C) de 30 à 75 % atomiques d'iridium ;

dans lequel une phase $L1_2$ a précipité dans une phase cubique à faces centrées de la phase matrice, et la quantité de la phase $L1_2$ est de 20 à 80 % en volume.

2. Superalloyage à température de fusion élevée selon la revendication 1, dans lequel le métal (B) est choisi parmi le titane, le zirconium, le hafnium, le vanadium, et le tantale.
3. Superalloyage à température de fusion élevée selon la revendication 1 ou 2, dans lequel le pourcentage atomique de la somme de (A) et de (B) est de 20 à 70 %.
4. Superalloyage à température de fusion élevée selon les revendications 1 à 3, dans lequel, au cas où le métal (C) est l'iridium, le rapport atomique de (A) à (B) est de 0,3/1 à 8/1.
5. Superalloyage à température de fusion élevée selon les revendications 1 à 3, dans lequel, au cas où le métal (C) est le rhodium, le rapport atomique de (A) à (B) est de 0,25/1 à 12/1.
6. Superalloyage à température de fusion élevée constitué de :

(A) 4 à 86 % atomiques de nickel,

(B) 0,5 à 20 % atomiques d'au moins un métal choisi dans le groupe constitué par le titane, le zirconium, le hafnium, le vanadium, le niobium, et le tantale, et

(C) 4 à 86 % atomiques d'iridium ou de rhodium, ou d'un mélange de ceux-ci, avec (D) de 0,4 à 20 % atomiques d'aluminium,

dans lequel une phase $L1_2$ a précipité dans une phase cubique à faces centrées de la phase matrice, et la quantité de la phase $L1_2$ est de 20 à 80 % en volume.

7. Superalloyage à température de fusion élevée selon la revendication 6, dans lequel les sommes des pourcentages atomiques de (A) et de (C), et de (B) et de (D) sont établies comme il suit,

$$(A) + (C) \geq 75 \% \text{ atomiques}$$

(B) + (D) ≤ 25 % atomiques.

8. Procédé pour produire un superalliage à température de fusion élevée selon l'une quelconque des revendications 1 à 5, lequel comprend la préparation d'un mélange d'au moins un parmi un superalliage à base d'iridium fabriqué à partir d'iridium en tant que base additionné d'au moins un métal choisi dans le groupe de métaux constitué par le titane, le zirconium, le hafnium, le vanadium, le niobium, et le tantale et un superalliage à base de rhodium fabriqué à partir de rhodium en tant que base additionné d'au moins un métal choisi dans le groupe de métaux décrit ci-dessus, avec du nickel, suivi de la formation de lingots pour produire un superalliage à température de fusion élevée.
9. Procédé pour produire un superalliage à température de fusion élevée selon l'une quelconque des revendications 1 à 7, lequel comprend la préparation d'un mélange d'au moins un parmi un superalliage à base d'iridium fabriqué à partir d'iridium en tant que base additionné d'au moins un métal choisi dans le groupe de métaux constitué par le titane, le zirconium, le hafnium, le vanadium, le niobium, et le tantale et un superalliage à base de rhodium fabriqué à partir de rhodium en tant que base additionné d'au moins un métal choisi dans le groupe de métaux décrit ci-dessus, avec un alliage à base de nickel fabriqué à partir de nickel en tant que base additionné d'au moins un métal choisi dans le groupe de métaux décrit ci-dessus, ou l'aluminium, suivi de la formation de lingots pour produire un superalliage à température de fusion élevée.

Fig. 1

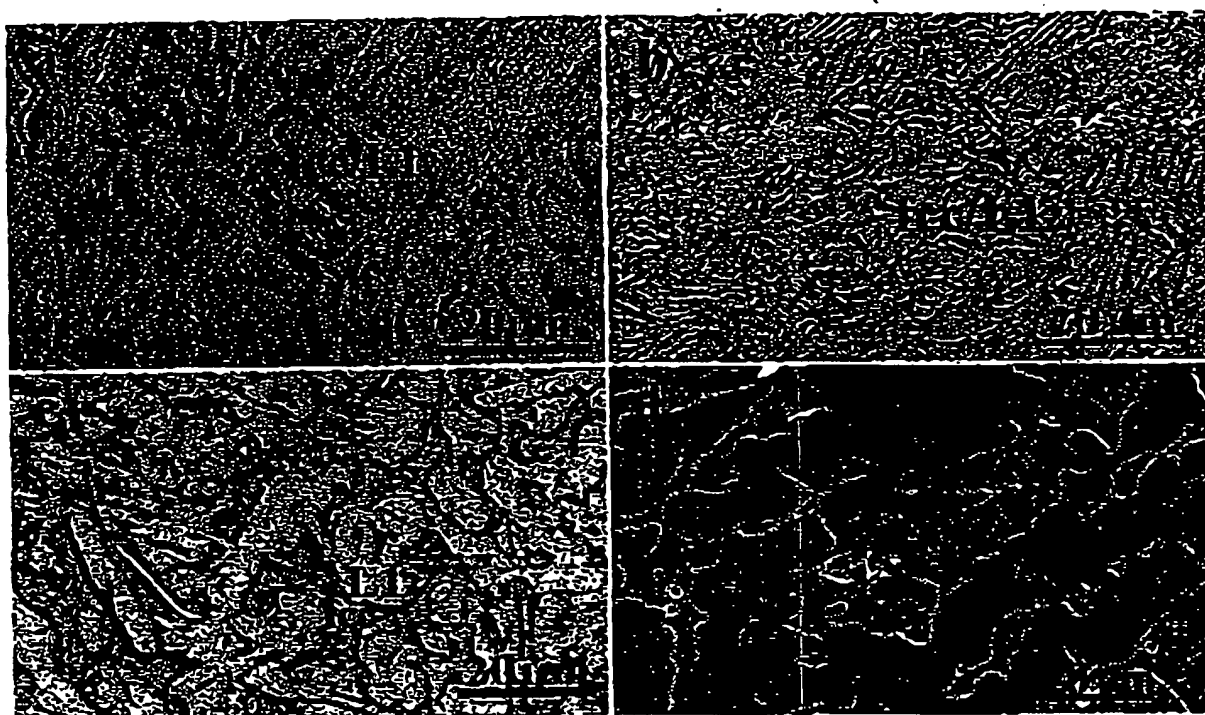


Fig. 2

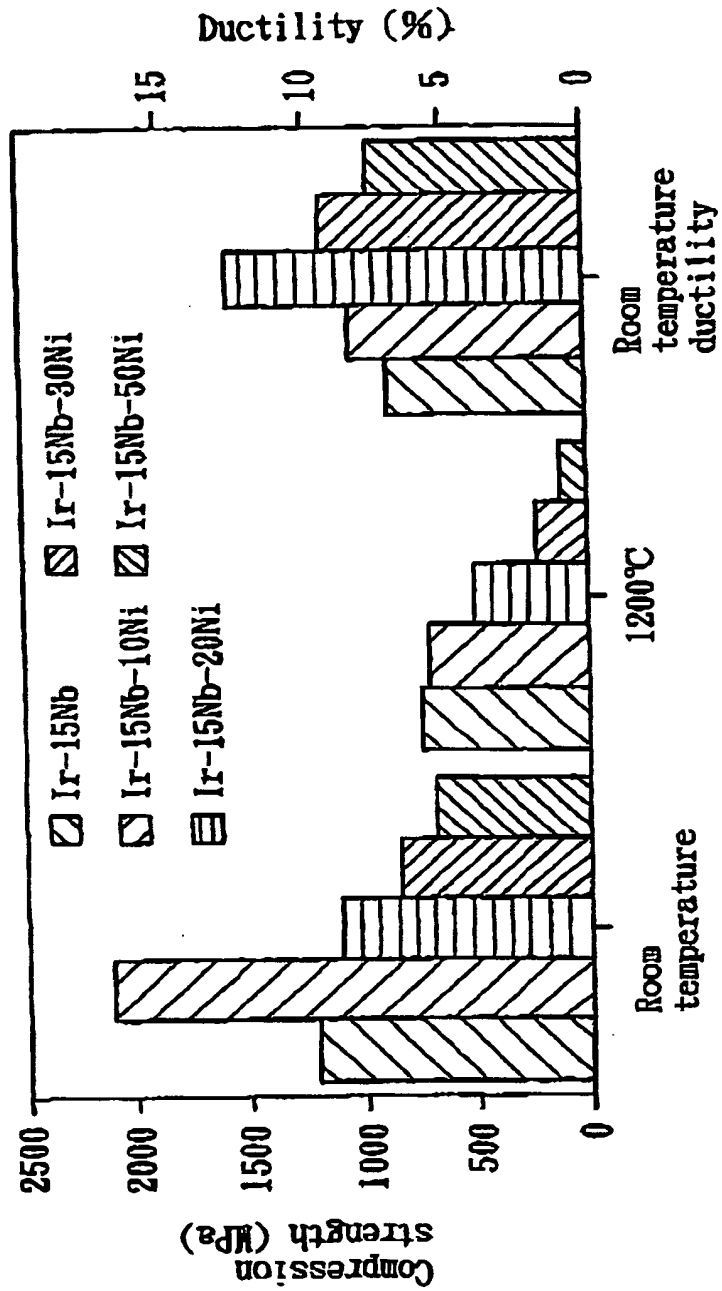




Fig. 3

Fig. 4

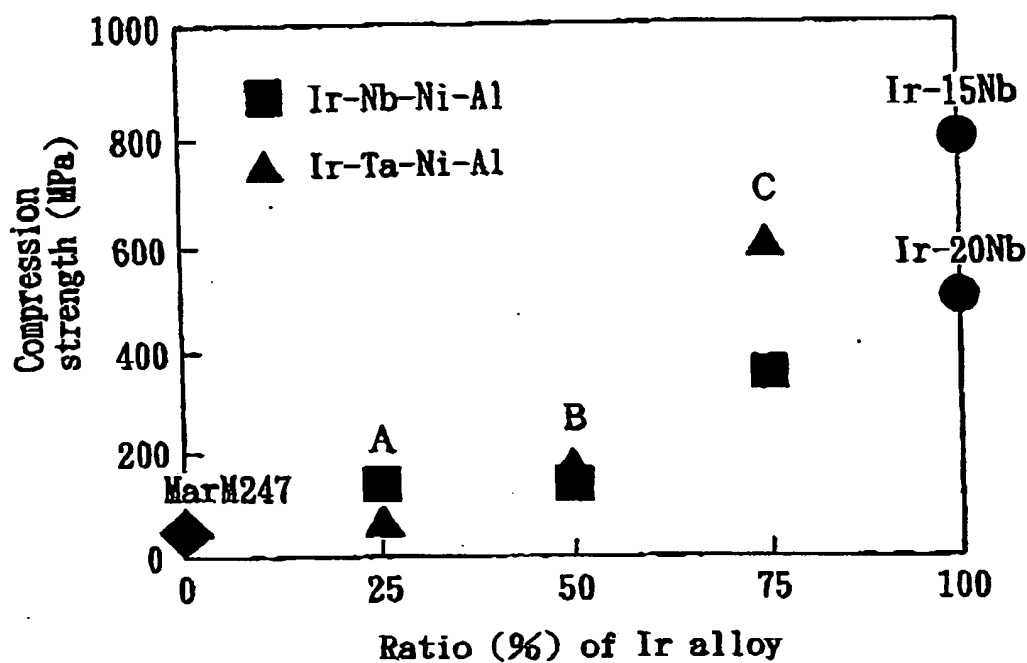


Fig. 5

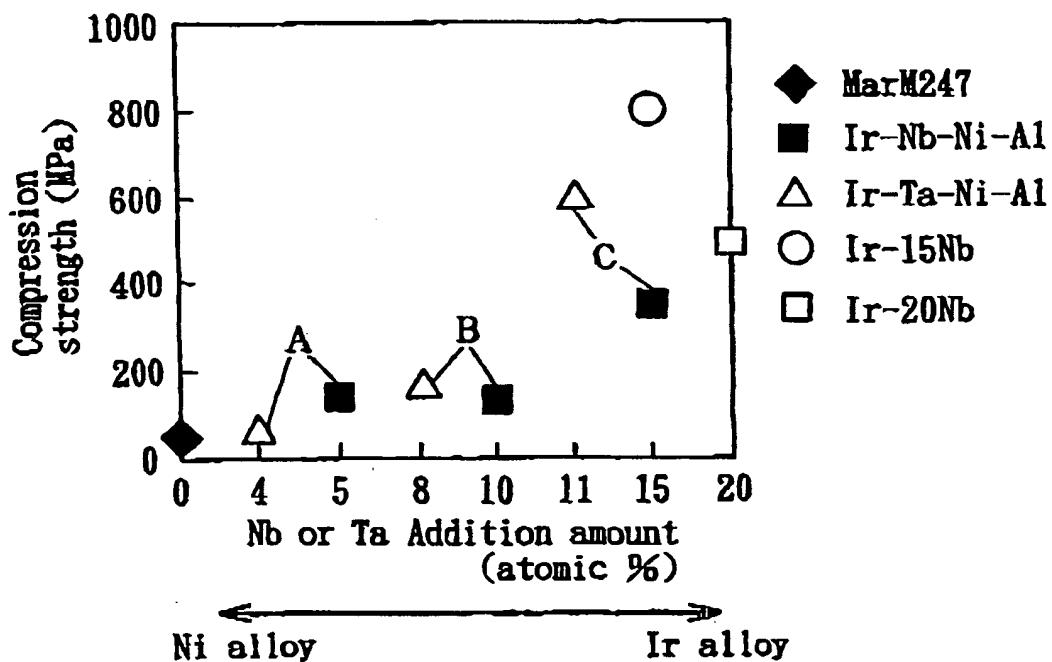


Fig. 6

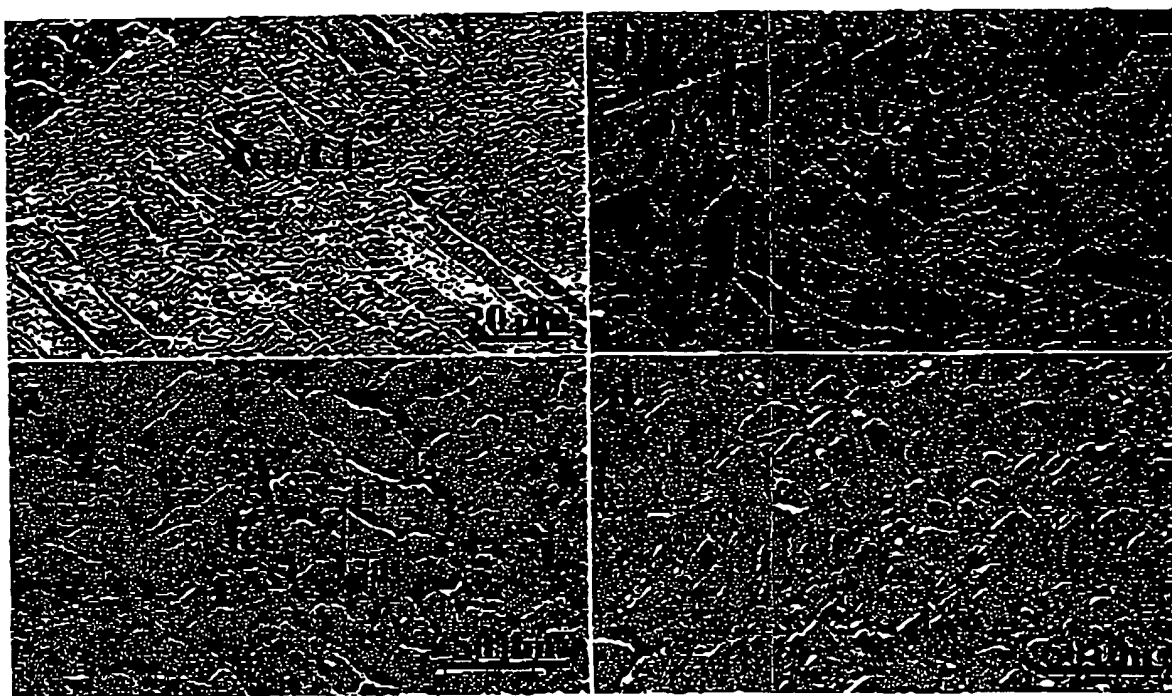


Fig. 7

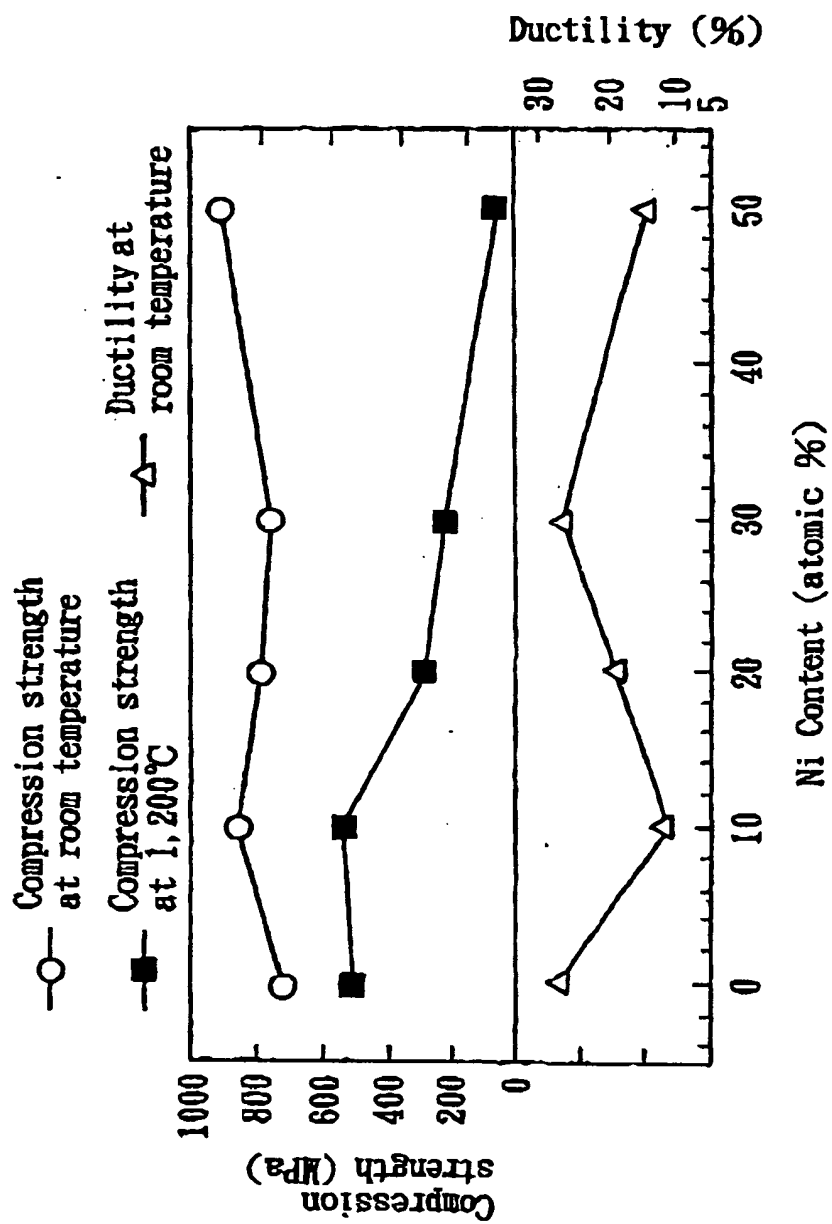


Fig. 8

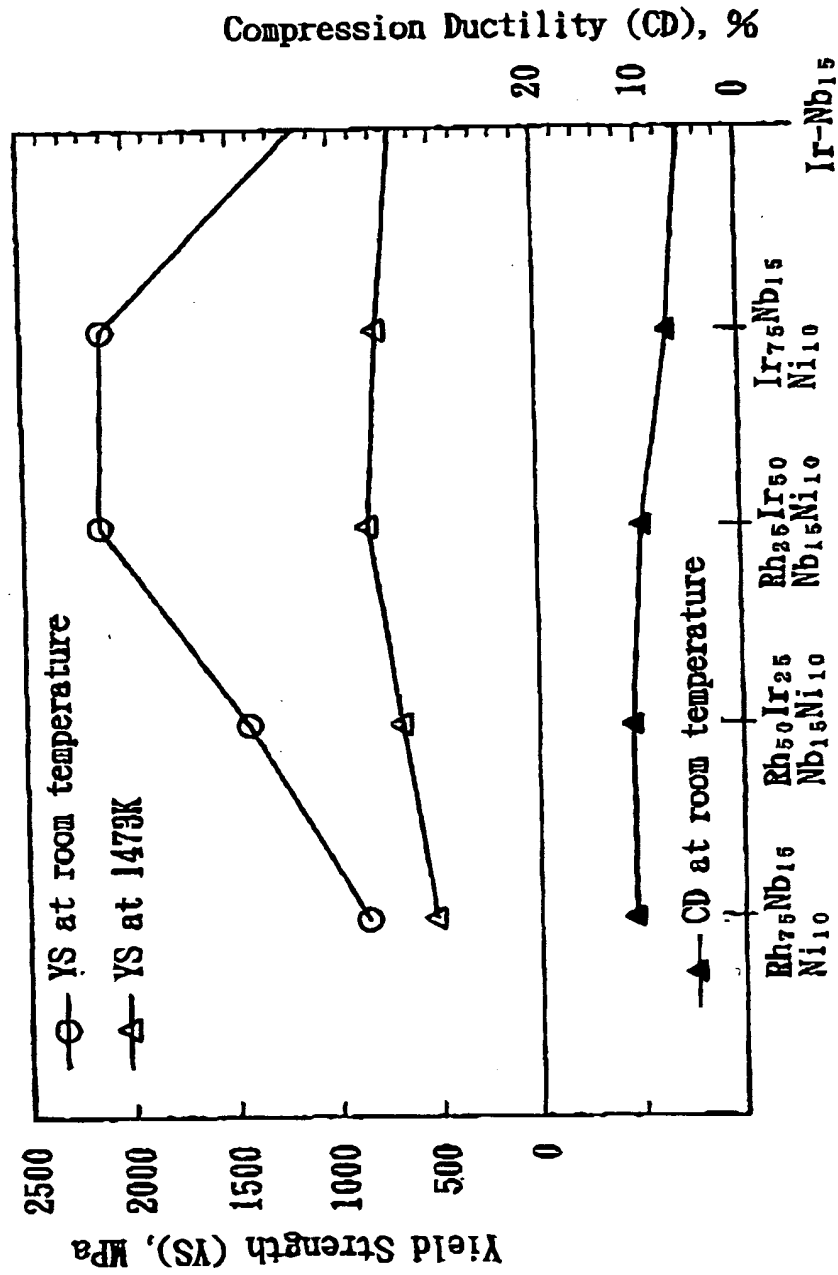


Fig. 9

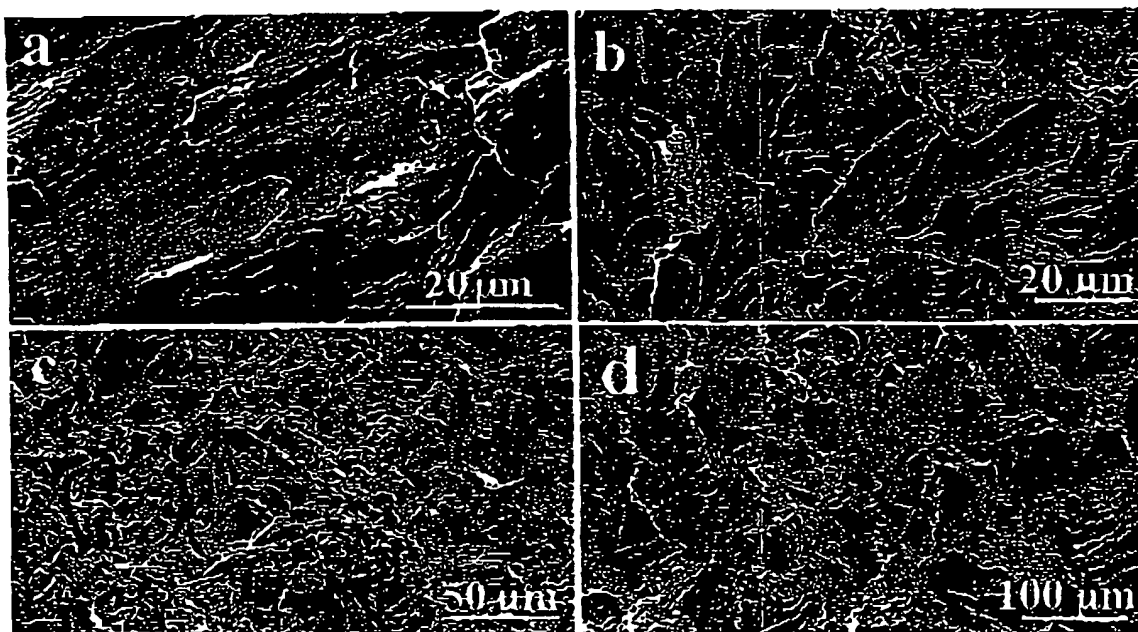
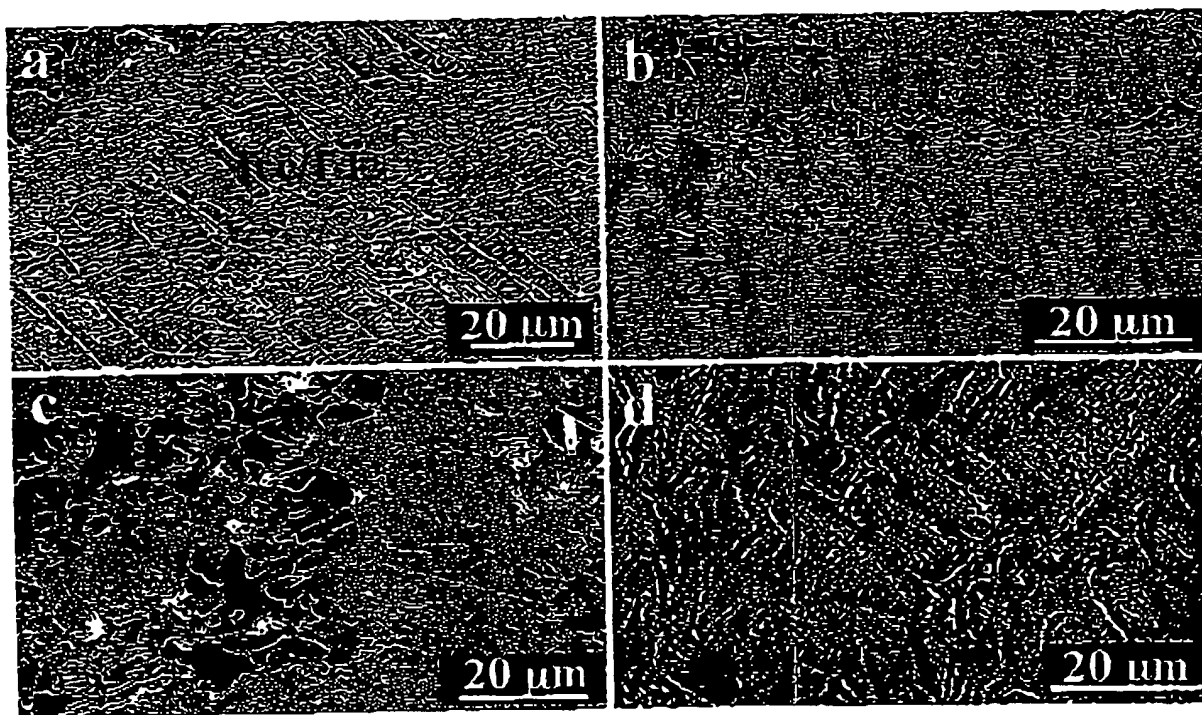


Fig. 10



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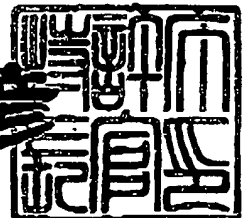
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【提出物件の目録】

【物件名】 明細書 1

【物件名】 図面 1

【物件名】 要約書 1

【ブルーフの要否】 要

【書類名】 明細書

【発明の名称】 高融点超合金とその製造方法

【特許請求の範囲】

【請求項 1】 イリジウム又はロジウムをベースに、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される 1 種以上の金属とともに、ニッケルを少なくとも含み、組織中に f c c 相及び L 1₂ 相の両相が少なくとも形成されていることを特徴としている高融点超合金。

【請求項 2】 f c c 構造を持つ母相中に L 1₂ 構造を持つ析出物が整合析出している請求項 1 記載の高融点超合金。

【請求項 3】 L 1₂ 相の体積%が 20～80%である請求項 1 又は 2 記載の高融点超合金。

【請求項 4】 イリジウムをベースに、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される 1 種以上の金属を 2～22 原子%添加したイリジウム基超合金、又はロジウムをベースに前記金属群から選択される 1 種以上の金属を 2～22 原子%添加したロジウム基超合金のいずれか一方、又はいずれか一方の超合金を実現する金属若しくは合金の組合せに、ニッケルを添加配合し、溶製して、請求項 1 乃至 3 いずれかに記載の高融点超合金を製造することを特徴とする高融点超合金の製造方法。

【請求項 5】 イリジウム基超合金又はロジウム基超合金に換算してその各々が少なくとも 5 モル%存在し、かつニッケルを少なくとも 5 原子%添加配合する請求項 4 記載の高融点超合金の製造方法。

【請求項 6】 イリジウムをベースに、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される 1 種以上の金属を 2～22 原子%添加したイリジウム基超合金、又はロジウムをベースに前記金属群から選択される 1 種以上の金属を 2～22 原子%添加したロジウム基超合金のいずれか一方、又はいずれか一方の超合金を実現する金属若しくは合金の組合せと、ニッケルをベースとするニッケル基合金又はこれを実現する金属若しくは合金の組合せとを混合し、溶製して、請求項 1 乃至 3 いずれかに記載の高融

点超合金を製造することを特徴とする高融点超合金の製造方法。

【請求項 7】 イリジウム基超合金、ロジウム基超合金、又はニッケル基合金に換算してその各々が少なくとも 5 モル%存在するように混合する請求項 6 記載の高融点超合金の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

この出願の発明は、高融点超合金とその製造方法に関するものである。さらに詳しくは、この出願の発明は、発電用ガスタービン、ジェットエンジン、ロケットエンジンなどの高温機器の出力及び熱効率をさらに向上させることのできる高融点超合金とこれを製造するための製造方法に関するものである。

【0002】

【従来の技術とその課題】

発電用ガスタービン、ジェットエンジン、ロケットエンジンなどの高温機器に用いられるタービンプレードやタービンペーンは高温・高応力下で使用される。従来、これらタービンプレードやタービンペーンには、高い耐熱性を有し、高温強度にも優れた Ni 基超合金が適用されているが、その使用温度は年々過酷になってきている。それと言うのも、燃焼ガス温度を高めることが、高温機器の出力及び熱効率をさらに高めるのに最も効果的な対応だからである。したがって、タービンプレードやタービンペーンには、高温強度を改善することが望まれ、これはとりもなおさず、タービンプレードやタービンペーンに適用される材料の高温強度の改善が必要不可欠であることを意味する。Ni 基超合金の実質的な強度を有する耐用温度はおよそ 1100℃である。この温度以上においても使用可能で、しかもそれを比較的安価に実現することのできる新しい材料が開発されれば、実用上きわめて有望である。

【0003】

この出願の発明は、以上の通りの事情に鑑みてなされたものであり、高温機器の出力及び熱効率をさらに向上させることのできる、従来の Ni 基超合金を上回る特性を有し、これを比較的安価に実現することも可能な、新しい高融点超合金

を提供することを目的としている。

【0004】

【課題を解決するための手段】

この出願の発明の発明者らは、上記の課題を解決すべく鋭意検討を加えたところ、融点が高く、高温で高強度を持ち、また、耐酸化性に優れたイリジウム基超合金（融点2447℃）又はロジウム基超合金（融点1960℃）と、これらに比べ軽量で延性に優れ、安価でもあるニッケル、又はニッケル基合金（密度 8.9g/cm^3 （cf. イリジウム基超合金： 22.4g/cm^3 、ロジウム基超合金： 12.44g/cm^3 ））を添加配合、又は混合し、溶製することにより、組織中に f c c 相及び $L1_2$ 相の両相が少なくとも形成し、場合によっては、f c c 構造を持つ母相中に $L1_2$ 構造を持つ析出物が整合析出した超合金が得られ、これらの超合金は、高温強度及び耐酸化性に優れるばかりでなく、比較的軽量で、延性をも有することを見出し、この出願の発明を完成したのである。

【0005】

すなわち、この出願の発明は、イリジウム又はロジウムをベースに、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される1種以上の金属とともに、ニッケルを少なくとも含み、組織中に f c c 相及び $L1_2$ 相の両相が少なくとも形成されていることを特徴としている高融点超合金（請求項1）を提供する。

【0006】

この出願の発明は、上記合金の好ましい態様として、f c c 構造を持つ母相中に $L1_2$ 構造を持つ析出物が整合析出していること（請求項2）、並びに $L1_2$ 相の体積%が20～80%であること（請求項3）を提供する。

またこの出願の発明は、イリジウムをベースに、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される1種以上の金属を2～22原子%添加したイリジウム基超合金、又はロジウムをベースに前記金属群から選択される1種以上の金属を2～22原子%添加したロジウム基超合金のいずれか一方、又はいずれか一方の超合金を実現する金属若しくは合金の組合せに、ニッケルを添加配合し、溶製して、請求項1乃至3いずれかに

記載の高融点超合金を製造することを特徴とする高融点超合金の製造方法（請求項4）を提供する。

【0007】

この請求項4に係る発明の好ましい態様として、この出願の発明は、イリジウム基超合金又はロジウム基超合金に換算してその各々が少なくとも5モル%存在し、かつニッケルを少なくとも5原子%添加配合すること（請求項5）を提供する。

さらにこの出願の発明は、イリジウムをベースに、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される1種以上の金属を2～22原子%添加したイリジウム基超合金、又はロジウムをベースに前記金属群から選択される1種以上の金属を2～22原子%添加したロジウム基超合金のいずれか一方、又はいずれか一方の超合金を実現する金属若しくは合金の組合せと、ニッケルをベースとするニッケル基合金又はこれを実現する金属若しくは合金の組合せとを混合し、溶製して、請求項1乃至3いずれかに記載の高融点超合金を製造することを特徴とする高融点超合金の製造方法（請求項6）を提供する。

【0008】

さらにまたこの出願の発明は、請求項6に係る発明の好ましい態様として、イリジウム基超合金、ロジウム基超合金、又はニッケル基合金に換算してその各々が少なくとも5モル%存在するように混合すること（請求項7）をも提供する。

以下、この出願の発明の高融点超合金とその製造方法についてさらに詳しく説明する。

【0009】

【発明の実施の形態】

この出願の発明の高融点超合金は、イリジウム又はロジウムをベースに、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される1種以上の金属とともに、ニッケルを少なくとも含む、3元系以上の多元合金であり、fcc相及びL1₂相の両相が少なくとも形成された組織を有する超合金である。

【0010】

この出願の発明の高融点超合金は、たとえば、イリジウムをベースに、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される1種以上の金属を2～22原子%添加したイリジウム基超合金、又はロジウムをベースに前記金属群から選択される1種以上の金属を2～22原子%添加したロジウム基超合金のいずれか一方、又はいずれか一方の超合金を実現する金属若しくは合金の組合せに、ニッケルを添加配合し、溶製することにより製造される。

【0011】

またこの出願の発明の高融点超合金は、イリジウムをベースに、チタン、ジルコニウム、ハフニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される1種以上の金属を2～22原子%添加したイリジウム基超合金、又はロジウムをベースに前記金属群から選択される1種以上の金属を2～22原子%添加したロジウム基超合金のいずれか一方、又はいずれか一方の超合金を実現する金属若しくは合金の組合せと、ニッケルをベースとするニッケル基合金又はこれを実現する金属若しくは合金の組合せとを混合し、溶製することによっても製造可能である。

【0012】

後者の製造方法において言及するニッケル基合金とは、ニッケル-アルミニウム (Ni-Al) 合金のような2元合金から現在耐熱材料として高温機器に適用されているより多元系のニッケル基超合金までを包含する。

上記製造方法において溶製は、その方式に特に制限はない。たとえば、アーク溶解、及びその後に行われる組成を均一化する均一化処理を一例として例示することができる。

【0013】

これらの製造方法により製造されるこの出願の発明の高融点超合金は、上記の通りに、組織中にfcc相及び L_{12} 相の両相を少なくとも有する。これら両相の形成により十分な強度が確保される。添加又は混合成分元素であるニッケルは、この組織において、イリジウム又はロジウムを一部置換していることが相組成

分析から確認される。

【0014】

また、これまでのところでは、超合金における各金属成分の組成比が大きな因子と考えられるが、fcc構造を持つ母相中に $L1_2$ 構造を持つ析出物が整合析出した二相整合組織が形成される場合もある。ここで、二相整合組織とは、隣接する結晶格子の並びが途切れずに連続している組織を言う。二相整合組織が形成されると、単にfcc相及び $L1_2$ 相の二相からなる超合金よりも強度が増大する。母相と析出物の間の整合界面が転位の移動を妨げるのがその原因ではないかと考えられる。このような二相整合組織は、後者の製造方法において原料に、イリジウム基超合金又はロジウム基超合金、及びニッケル基合金を母合金として用い、しかもそれぞれが上記二相整合組織を持つ場合により確実に形成される。

【0015】

fcc相及び $L1_2$ 相は、必ずしも各々が1種類ずつである必要はない。この出願の発明の高融点超合金は、上記の通りの多元合金であるため、濃度の異なる数種類のfcc相と $L1_2$ 相が混在することも可能である。

これらfcc相及び $L1_2$ 相の両相が形成した組織において、 $L1_2$ 相は、体積率で20～80%とするのが好ましい。下限を下回る場合には強度の低下が見られる。一方、上限はこれを上回っても構わないが、そのような超合金を作製するのはかなり難しくなる。

【0016】

そして、この出願の発明の高融点超合金は、母合金として用いる場合のイリジウム基超合金又はロジウム基超合金と、ニッケル又はニッケル基合金の特性をそれぞれ独立して発現する。つまり、この出願の発明の高融点超合金は、イリジウム基超合金及びロジウム基超合金が持つ高融点、高温高強度、及び優れた耐酸化性とともに、ニッケル又はニッケル基合金が持つ軽量かつ優れた延性を全て示すのである。また、ニッケル又はニッケル基合金の存在によってこの出願の発明の高融点超合金は、比較的安価ともなる。

【0017】

ただ、これらの金属、合金、そして超合金の各特性が明らかに認められるよう

になるには、イリジウム基超合金又はロジウム基超合金に換算してその各々が少なくとも5モル%存在し、かつニッケル単体、又はニッケル基合金に換算してその含有量を少なくとも5モル%とするのが好ましい。この下限値未満の場合には、特性が必ずしも十分に発現されるとは限らない。

【0018】

イリジウム基超合金又はロジウム基超合金それ自体の、又はこれらに換算して含有量が5～50モル%を含むこの出願の発明の高融点超合金は、軽量であり、タービンプレード等の回転部材として有効と考えられ、一方、含有量がそれよりも多い50～95%の場合には、より高温で使用される部材への適用が有望視される。

【0019】

次にこの出願の発明の高融点超合金とその製造方法の実施例を示す。

【0020】

【実施例】

(実施例1)

イリジウム-15ニオブ (Ir-15Nb) 合金及びニッケル (Ni) を配合し、真空炉中でアルゴン雰囲気下にアーク溶解して、表1に示した組成を有するA、B、C、及びDの4種類の超合金 (インゴット) を製造した。

【0021】

【表1】

| 超合金 | 超合金組成 (at%) | | |
|-----|-------------|----|----|
| | Ni | Nb | Ir |
| A | 10 | 15 | 残 |
| B | 20 | 15 | 残 |
| C | 30 | 15 | 残 |
| D | 50 | 15 | 残 |

【0022】

このインゴットから高さ6mm、直径3mmの供試片を切り出し、これを、 5×10^{-7} torrの真空炉内で1300℃、1週間の時効処理を行った。そして、供試片に形成した相をX線回折分析(XRD)及びエネルギー分散型X線分析器(EDAX)で決定した。

その結果、表1の超合金A及びBは、fcc相及び $L1_2$ 相の二相のみからなる組織を有していた。特に、超合金Aには、fcc構造を持つ母相中に $L1_2$ 構造を持つ析出物が整合析出した二相整合組織が形成されていた。fcc相はIrからなり、 $L1_2$ 相は Ir_3Nb からなっていた。また、これらいずれにもNiが固溶していた。一方、超合金C及びDは、上記二相の他に、斜方晶系に属する δ 相($(Ir, Ni)_{11}Nb_9$)が第三の相として確認された。なお、いずれの超合金においても $L1_2$ 構造を持つ Ir_3Nb は、体積率で20~80%の範囲内に収まっていた。

【0023】

図1a~dは、各々、供試片の光学顕微鏡写真である。

超合金Aでは樹枝状組織(図1a)が、超合金B、C、及びDでは微細組織(図1b、c、及びd)が形成している。また、Niの配合量が増加するにしたがって組織が厚く、粗くなっていることも確認される。

そして、上記供試材について、圧縮試験(大気中、応力速度 $3.0 \times 10^{-4} s^{-1}$)を室温から1200℃までにおいて行った。その結果を示したのが図2のグラフである。

【0024】

この図2のグラフから明らかなように、超合金Aの圧縮強度は、室温ではIn-15Nbのほぼ2倍であり、1200℃ではIn-15Nbと同等である。超合金B、C、及びDの圧縮強度は、室温及び1200℃ともにIn-15Nbの圧縮強度を下回る。だが、いずれの超合金の圧縮強度も、高温機器に適用されていたNi基超合金よりは高い。

【0025】

また、いずれの超合金においてもNiの添加により延性が改善されている。特

に、超合金Bは、およそ13%であり、Ir-15Nbの延性をはるかに凌いでいる。Ir-15Nb合金よりも実用性が高いと認められる。しかもNiは、Irを一部置換するため、超合金中のIr量を低減することができ、低価格化が図られる。この点においても実用性の高さが確認される。

(実施例2)

イリジウム基超合金としてイリジウム-20ニオブ (Ir-20Nb) 合金及びイリジウム-20タンタル (Ir-20Ta) 合金を、また、ニッケル基合金としてニッケル-16.8アルミニウム (Ni-16.8Al) 合金を選択した。これらイリジウム基超合金及びニッケル基合金をモル分率を、Ir基超合金: Ni基超合金=25:75 (A群)、50:50 (B群)、75:25 (C群) とし、合計6種類の以下の表2に示す組成の4元合金をアルゴン雰囲気中でアーク溶解により作製した。

【0026】

【表2】

| | 超合金組成 (at%) | |
|----|----------------------|-------------------------|
| A群 | Ir-5Nb-62.4Ni-12.6Al | Ir-3.75Ta-62.4Ni-12.6Al |
| B群 | Ir-10Nb-41.6Ni-8.4Al | Ir-7.5Ta-41.6Ni-8.4Al |
| C群 | Ir-15Nb-20.8Ni-4.2Al | Ir-11.25Ta-20.8Ni-4.2Al |

【0027】

これら6種類の4元合金について、実施例1と同様の相決定及び組織観察を行った。

その結果、A群及びC群の4種類の超合金には、fcc相 (Ir, Ni) と2種類のL1₂相 (Ni, Ir)₃ (Al, Nb) 及び (Ir, Ni)₃ (Nb, Al)、又は (Ni, Ir)₃ (Al, Ta) 及び (Ir, Ni)₃ (Ta, Al) からなる二相整合組織が形成していた。一方、B群の2種類の超合金では、A群及びC群の超合金と同じfcc相と2種類のL1₂相による二相整

合組織が形成されていたが、B2相 ($(\text{Ir}, \text{Ni}) (\text{Al}, \text{Nb})$) 又は ($\text{Ir}, \text{Ni}) (\text{Al}, \text{Ta})$) が他に認められた。

【0028】

なお、上記組成式において、たとえば、 $(\text{Ni}, \text{Ir})_3 (\text{Al}, \text{Nb})$ は、 Ir 及び Nb を含有する $\text{Ni}_3 \text{Al}$ で、 Ir が Ni を、また、 Nb が Al をそれぞれ一部置換していることを意味している。他の組成式も同様の標記方式を採用している。

図3a～cは、各々、A群、B群、及びC群に属する In-Nb-Ni-Al 4元合金の組織を示した二次電子像である。

【0029】

超合金Aでは、fcc相、及び Ir 及び Nb を含む $\text{Ni}_3 \text{Al}$ の第1の $\text{L}1_2$ 相が観察された。超合金B及びCでは、より大きな $\text{L}1_2$ 相が析出している。B2相は、上記の通りに、超合金Bのみに観察された。これら3つの超合金A～Cでは、 Ir 及び Nb を含む $\text{Ni}_3 \text{Al}$ の第1の $\text{L}1_2$ 相とともに、 Ni 及び Al を含む $\text{Ir}_3 \text{Nb}$ の小さな第2の $\text{L}1_2$ 相が、fcc母相の中に確認された。

【0030】

次いで、作製した合金を真空中1300℃及び1400℃で1週間時効処理を行い、再び、組織観察した。

1300℃の時効処理を行った超合金には、2種類の小さな第2の $\text{L}1_2$ 相がfcc母相から析出した。超合金B及びCの相解析の結果、この第2の $\text{L}1_2$ 相は、第1の $\text{L}1_2$ 相よりも Ni を多く含んでいることが確認された。超合金Aでは、第1の $\text{L}1_2$ 相には23at%の Ir が含まれていた。母相中の Ir 量は、超合金の Ir 量に伴って増加する。一方、母相中の Nb 量は、ほぼ5at%のレベルにある。1400℃の時効処理後には、より大きな第1の $\text{L}1_2$ 相に加え、fcc相中に異なる形状及びサイズの第2の $\text{L}1_2$ 相が多量に形成した。また、超合金Bでは、B2相が消失した。このことから、超合金BにおけるB2相の融点が1400℃であると考えられる。そして、いずれの超合金においても $\text{L}1_2$ 相は、体積率で20～80%の範囲内に収まっていた。

【0031】

以上の組織観察結果は、In-Ta-Ni-Al 4元合金についても同様であった。

次いで、上記6種類の4元合金を1400℃に1週間加熱し、1200℃における圧縮強度を測定した。その結果を示したのが、図4及び図5の相関図である。

これら図4及び図5図中には、比較のために、従来のNi基超合金(MarM 247)、及びIr-15Nb、Ir-20Nbのイリジウム基超合金の強度も合わせて示した。

【0032】

4元合金のいずれも、高温機器に適用されていたNi基超合金に比べ、高い圧縮強度を示した。一方、これら4元合金の圧縮強度は、Ir-Nbよりも低い。しかしながら、延性は、ニッケル基合金の混合により、最低でも18%、最高で89%が得られ、改善されている。Ir-15Nbよりも実用性が高いと認められる。

【0033】

また、図4からは、4元合金の圧縮強度は、イリジウム基超合金の添加成分であるNb又はTaの添加量が多くなるにつれて増大することも確認される。

(実施例3)

$Rh_{85-X}Nb_{15}Ni_X$ ($X=10, 20, 30, 50$) の組成を有する4つの試料をアーク溶解により作製し、各々のインゴットから高さ6mm、直径3mmの供試片を切り出した。この供試片には、真空中 ($<10^{-5}Pa$) において1200℃、100時間の時効処理を行った。そして、圧縮試験(大気中、応力速度 $3.0 \times 10^{-4} s^{-1}$) を20~1200℃において行った。試験中に均一な温度分布が得られるように、各供試片を炉中で12~20分間試験温度まで加熱し、負荷開始前に5分間その温度に保持した。圧縮強度は、試験前後の供試材の高さの変化から算出した。

【0034】

また、超合金の組織を走査電子顕微鏡(SEM)及び透過型電子顕微鏡(TEM)により観察した。走査電子顕微鏡観察を行った供試片については、5% HClのエチルアルコール溶液で電子研磨した。熱処理後の超合金の結晶構造及び相

組成は、X線回折分析（XRD）及びエネルギー分散型X線分析器（EDAX）で決定した。

【0035】

$X \leq 30$ の $Rh_{85-X}Nb_{15}Ni_X$ 超合金は、fcc相と、Niを含む Rh_3Nb の $L1_2$ 相の二相のみからなる組織を有していた。特に、 $X=10$ の $Rh_{75}Nb_{15}Ni_{10}$ 超合金には、fcc構造を持つ母相中に $L1_2$ 構造を持つ析出物が整合析出した二相整合組織が形成されていた。一方、 $X=50$ の $Rh_{35}Nb_{15}Ni_{50}$ 超合金には、斜方晶系に属する γ'' 相（ $(Ni, Rh)_3Nb$ ）も確認された。 Rh_3Nb に含まれるNiの含有量は、 $Rh_{75}Nb_{15}Ni_{10}$ （ $X=10$ ）の4.8at%から $Rh_{35}Nb_{15}Ni_{50}$ （ $X=50$ ）の19.6at%までであった。また、いずれの超合金においても $L1_2$ 相は、体積率で20～80%の範囲内に収まっていた。

【0036】

図6は、1200℃で100時間熱処理した超合金の顕微鏡写真である。

図6のa～dは、各々、 $Rh_{85-X}Nb_{15}Ni_X$ （ $X=10, 20, 30, 50$ ）の組成に対応しているが、いずれの超合金においても樹枝状組織が形成している。また、これらa～dの比較から、実施例1と同様に、Niの配合量が増加するにしたがって組織が粗くなっていることが確認される。

【0037】

図7は、 $Rh_{85-X}Nb_{15}Ni_X$ 超合金の圧縮強度及び延性をNiの含有量との関係において示した相関図である。この図7には、比較のために、 $Rh-15at\%Nb$ 合金のデータも合わせて示している。

室温では、Niを添加した超合金は、 $Rh-Nb$ 二相合金に比べ高い圧縮強度を示す。1200℃では、 $Rh_{75}Nb_{15}Ni_{10}$ （ $X=10$ ）が473MPaと、 $Rh-Nb$ 二相合金の圧縮強度を上回るが、Niの含有量の増加につれて低下する。だが、いずれの超合金の圧縮強度は、高温機器に適用されていたNi基超合金よりは高い。

【0038】

室温延性についても、Niを添加した超合金は、 $Rh_{55}Nb_{15}Ni_{30}$ （ $X=3$

0) の組成において $Rh-Nb$ 二相合金に匹敵するものの、これ以外では低い値を示す。しかしながら、最低でも 11% ($Rh_{75}Nb_{15}Ni_{10}$ ($X=10$)) であり、実施例 1 に示した In ベースの超合金以上の室温延性を有する。

(実施例 4)

実施例 2 において、イリジウムに代え、ロジウムを超合金の構成成分に採用した他は、同様に超合金を作製し、その相決定及び組織観察とともに、圧縮強度及び延性を測定した。イリジウムについての実施例 2 とほぼ同様に、高温機器に適用されていた Ni 基超合金に比べ、高い圧縮強度を示すとともに、延性が改善されてもいる。

【0039】

もちろんこの出願の発明は、以上の実施例によって限定されるものではない。超合金の組成、配合割合、作製方法等の細部については様々な態様が可能であることは言うまでもない。

【0040】

【発明の効果】

以上詳しく説明した通り、この出願の発明によって、 Ni 基超合金を上回る特性を有し、これを比較的安価に実現することもできる、新しい高融点超合金が提供される。高温機器の出力及び熱効率のさらなる向上が実現可能となる。

【図面の簡単な説明】

【図 1】

a、b、c、及び d は、各々、実施例 1 における供試材の組織を示した光学顕微鏡写真である。

【図 2】

実施例 1 における供試材の圧縮強度及び延性を $In-15Nb$ とともに比較した棒グラフである。

【図 3】

a、b、及び c は、各々、実施例 2 における $In-Nb-Ni-Al$ 4 元合金の組織を示した二次電子像である。

【図 4】

イリジウム基超合金のモル分率と実施例 2 で作製した超合金の圧縮強度との相関関係を示した相関図である。

【図 5】

イリジウム基超合金におけるニオブ又はタンタルの添加量と実施例 2 で作製した超合金の圧縮強度との相関関係を示した相関図である。

【図 6】

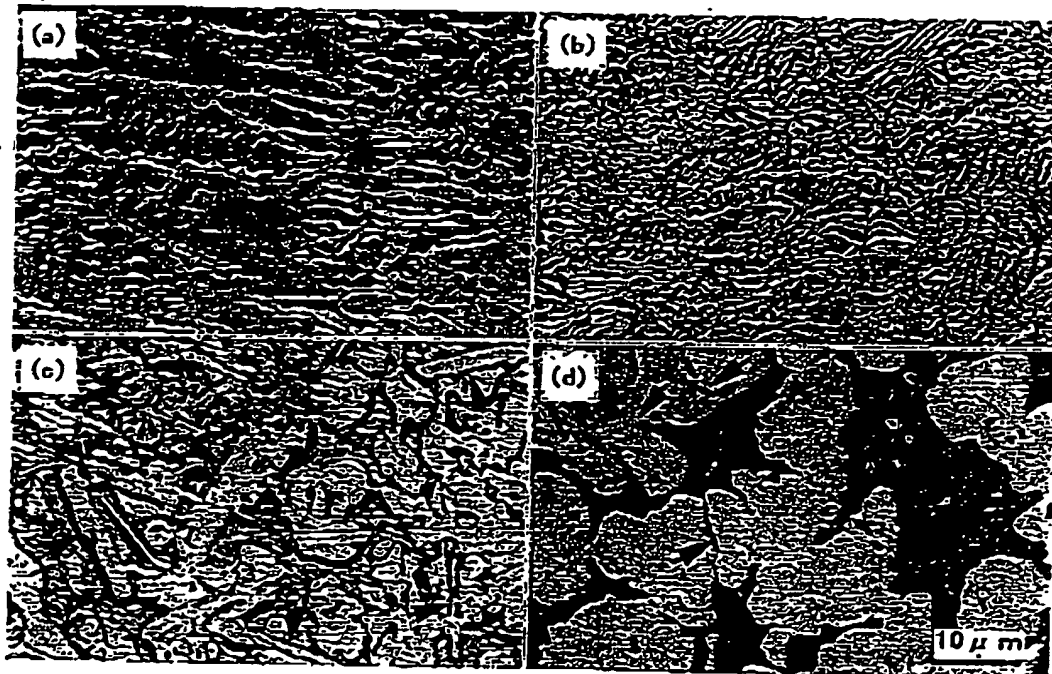
a、b、c、及び d は、各々、実施例 3 における供試材の組織を示した顕微鏡写真である。

【図 7】

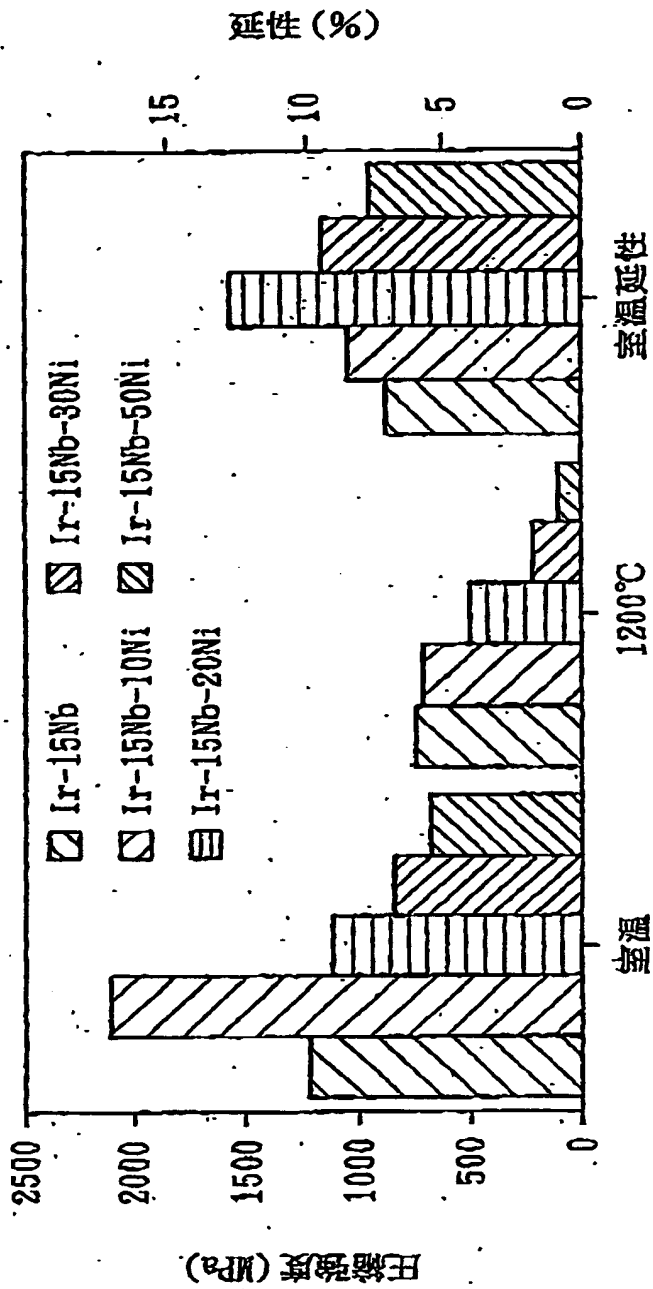
実施例 3 で作製した超合金におけるニッケルの含有量と圧縮強度及び延性との相関関係を示した相関図である。

【書類名】 図面

【図 1】



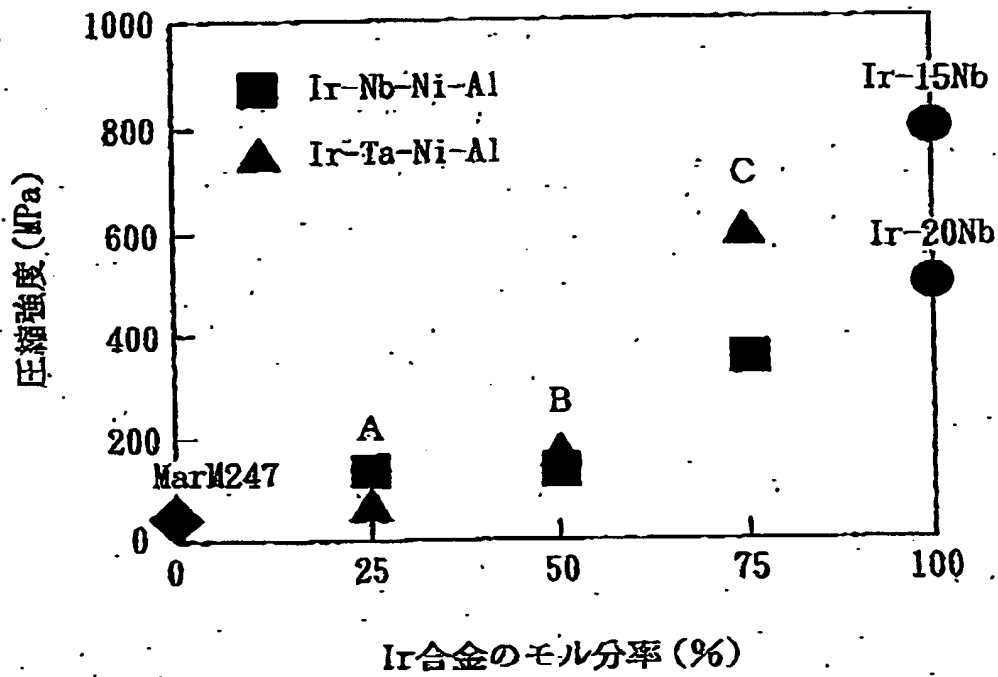
【図2】



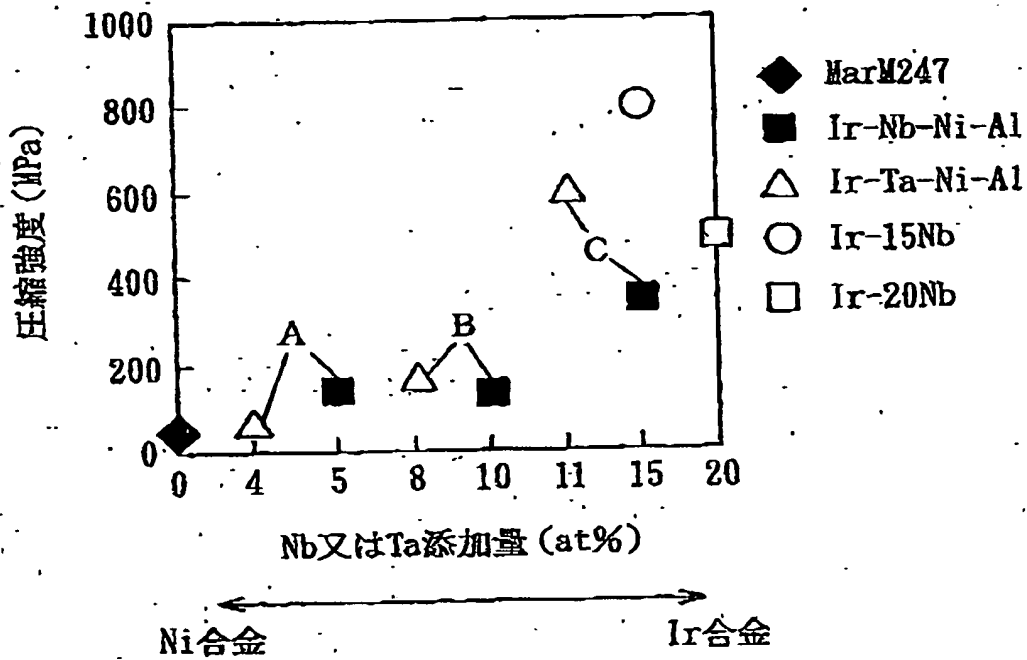
【図3】



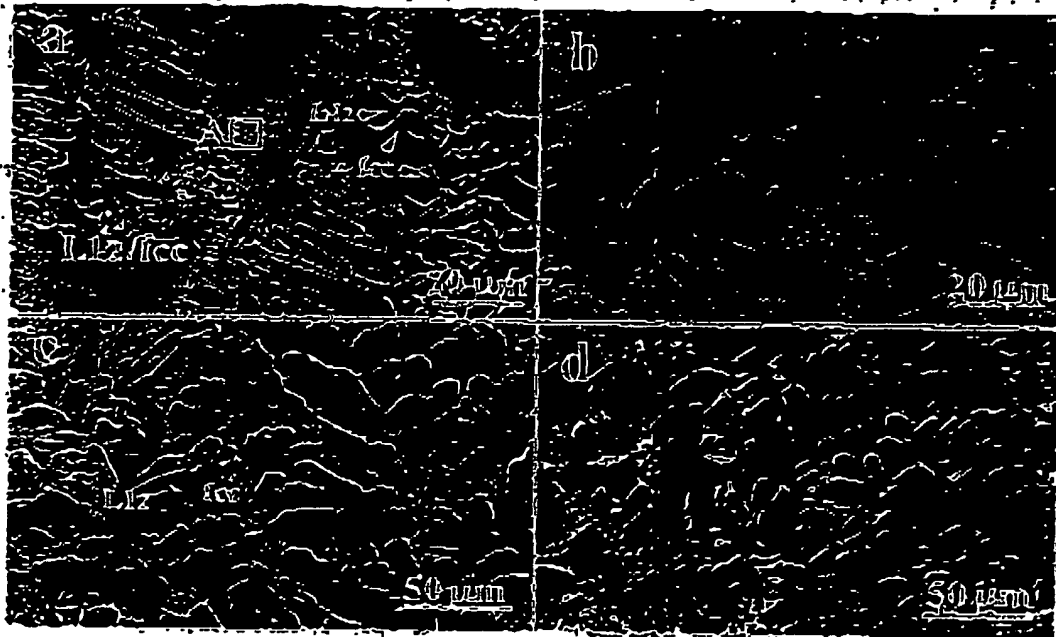
【図4】



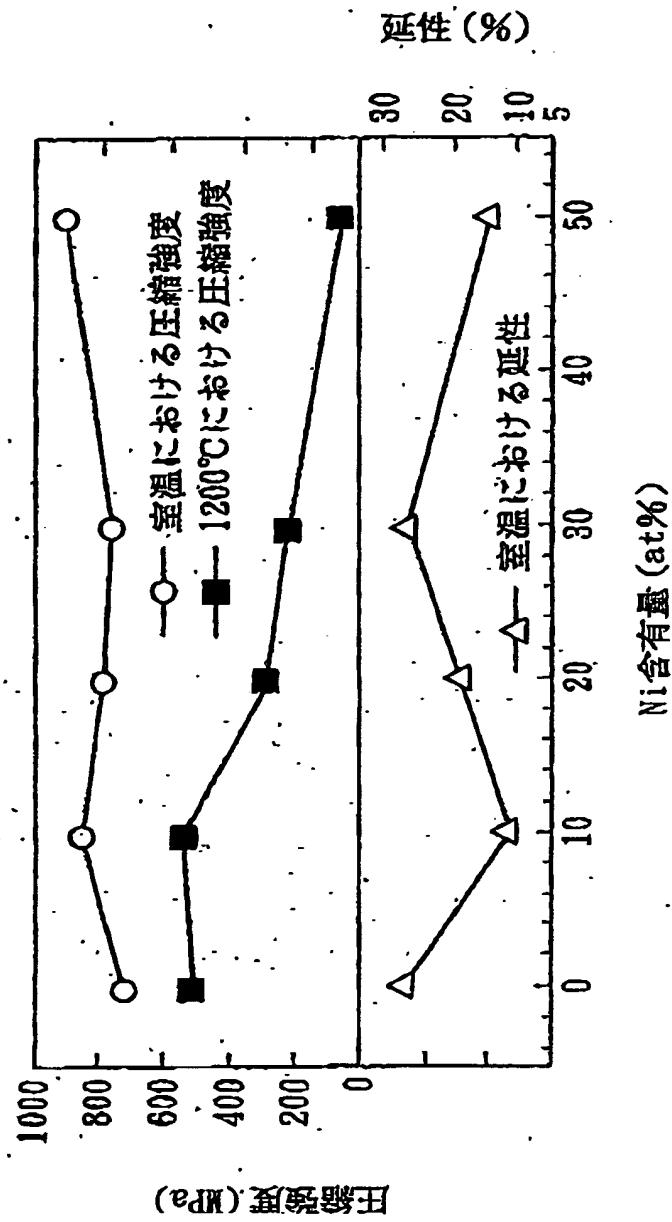
【図5】



【図 6】



【図7】



【書類名】 要約書

【要約】

【課題】 Ni 基超合金を上回る特性を有し、これを比較的安価に実現すること
も可能な、新しい高融点超合金を提供する。

【解決手段】 イリジウム又はロジウムをベースに、チタン、ジルコニウム、ハ
フニウム、バナジウム、ニオブ、及びタンタルからなる金属群から選択される 1
種以上の金属とともに、ニッケルを少なくとも含み、組織中に f c c 相及び L 1
2 相の両相が少なくとも形成されている。

【選択図】 図 1

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